

**Supporting Information for**  
***o*-Quinone Methide with Overcrowded Olefin Component as a Dehydration Catalyst under**  
**Aerobic Photoirradiation Conditions**

Daisuke Uraguchi<sup>1</sup>, Kohsuke Kato<sup>2</sup>, Takashi Ooi<sup>\*2</sup>

<sup>1</sup>*Institute for Catalysis, Hokkaido University, Sapporo 001-0021, Japan*

<sup>2</sup>*Institute of Transformative Bio-Molecules (WPI-ITbM) and Department of Molecular and Macromolecular Chemistry  
Graduate School of Engineering, Nagoya University, Nagoya 464-8601, Japan*

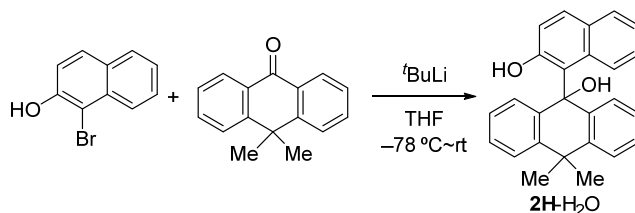
[tooi@chembio.nagoya-u.ac.jp](mailto:tooi@chembio.nagoya-u.ac.jp)

**General Information:** Infrared spectra were recorded on a SHIMADZU IRAffinity-1 spectrometer. <sup>1</sup>H NMR spectra were recorded on a JEOL JNM-ECZ400S (400 MHz), JEOL JNM-ECA500II (500 MHz), or JEOL JNM-ECA600II (600 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance (CD<sub>3</sub>CN: 1.94 ppm, C<sub>6</sub>D<sub>6</sub>: 7.16 ppm) or tetramethylsilane (0.00 ppm; CDCl<sub>3</sub>) resonance as the internal standard. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, brd = broad-doublet), and coupling constants (Hz). <sup>13</sup>C NMR spectra were recorded on a JEOL JNM-ECA600II (151 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance (CDCl<sub>3</sub>: 77.16 ppm, CD<sub>3</sub>CN: 1.32 ppm, C<sub>6</sub>D<sub>6</sub>: 128.06 ppm). <sup>19</sup>F NMR spectra were recorded on a JEOL JNM-ECZ400S (376 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from benzotrifluoride (−64.0 ppm) resonance as the external standard. The high-resolution mass spectrometry were conducted on Thermo Fisher Scientific Exactive (ESI). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 F<sub>254</sub>, 0.25 mm). Flash column chromatography was performed on Silica gel 60N (spherical neutral, 40-50 μm; Kanto Chemical Co., Inc.).

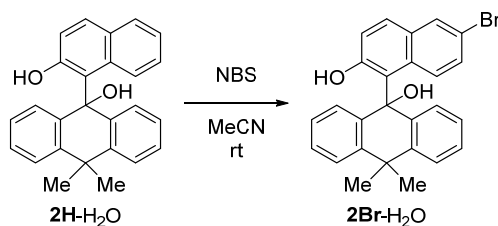
Dichloromethane was supplied from Kanto Chemical Co., Inc. Other simple chemicals were purchased and used as such.

## Experimental Section:

### Synthesis and Characterization of Quinone Methides and Their Precursors:

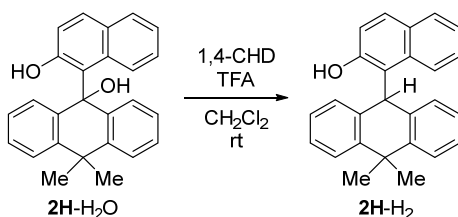


**Preparation of 9-(2-hydroxynaphthalen-1-yl)-10,10-dimethyl-9,10-dihydroanthracen-9-ol (2H-H<sub>2</sub>O):** To a solution of 1-bromo-2-naphthol (1.78 g, 8.0 mmol) in anhydrous tetrahydrofuran (THF) (27.0 mL) was added <sup>t</sup>BuLi (1.6 M in <sup>n</sup>pentane, 15.0 mL, 24.0 mmol) dropwise at -78 °C and the reaction mixture was stirred at -15 °C for 1 h. A solution of 10,10-dimethylanthrone (1.67 g, 7.5 mmol) in anhydrous THF (8.0 mL) was introduced dropwise to the mixture at -78 °C, and the resulting mixture was allowed to warm to room temperature and stirred there for overnight. The reaction mixture was poured into a saturated aqueous solution of NH<sub>4</sub>Cl and extracted with ethyl acetate (EA) three times. The combined organic extracts were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of volatiles under reduced pressure, purification of the residue was performed by column chromatography on silica gel (hexane (H)/EA = 10:1 as eluent) to afford **2H-H<sub>2</sub>O** in 77% yield (2.11 g, 5.8 mmol) as a white solid. **2H-H<sub>2</sub>O**: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 11.09 (1H, s), 7.74 (1H, d, *J* = 7.8 Hz), 7.68 (2H, d, *J* = 7.8 Hz), 7.61 (1H, d, *J* = 7.8 Hz), 7.35 (2H, dt, *J* = 1.5, 7.8 Hz), 7.28 (2H, dd, *J* = 1.5, 7.8 Hz), 7.25 (1H, d, *J* = 7.8 Hz), 7.08 (2H, t, *J* = 7.8 Hz), 7.00 (1H, t, *J* = 7.8 Hz), 6.91 (1H, d, *J* = 7.8 Hz), 6.78 (1H, dt, *J* = 1.2, 7.8 Hz), 2.83 (1H, s), 1.98 (3H, s), 1.80 (3H, s); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 156.8, 142.3, 138.5, 131.1, 130.7, 129.7, 129.1, 128.6, 128.5, 127.5, 127.2, 125.6, 125.3, 122.2, 120.7, 117.9, 81.2, 38.0, 36.9, 31.8; IR (film) 3100, 1653, 1506, 1457, 1224, 1153, 1068, 1038, 1003, 981 cm<sup>-1</sup>; HRMS (ESI) Calcd for C<sub>26</sub>H<sub>21</sub>O<sub>2</sub><sup>-</sup> ([M-H]<sup>-</sup>) 365.1536. Found 365.1545.

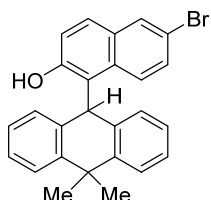


**Preparation of 9-(6-bromo-2-hydroxynaphthalen-1-yl)-10,10-dimethyl-9,10-dihydroanthracen-9-ol (2Br-H<sub>2</sub>O):** To a solution of **2H-H<sub>2</sub>O** (109.9 mg, 0.30 mmol) in acetonitrile (MeCN) (3.0 mL) was added *N*-bromosuccinimide (NBS) (53.4 mg, 0.30 mmol). After being stirred at room temperature for 24 h, the resulting mixture was diluted with water and extracted with EA three times. The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure to afford the crude residue. Purification of the residue by column chromatography on silica gel (H/EA = 10:1 as eluent) furnished **2Br-H<sub>2</sub>O** in 34% yield (45.4 mg, 0.10 mmol) as a light-purplish solid. **2Br-H<sub>2</sub>O**: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 11.10 (1H, s), 7.75 (1H, d, *J* = 2.4 Hz), 7.68 (2H, d, *J* = 8.1 Hz), 7.65 (1H, d, *J* = 8.1 Hz), 7.37 (2H, dt, *J* = 1.5, 8.1 Hz), 7.27 (1H, d, *J* = 8.1 Hz), 7.25 (2H, d, *J* = 8.1 Hz), 7.10 (2H, t, *J* = 8.1 Hz), 6.86 (1H, dd, *J* = 2.4, 8.1 Hz), 6.79 (1H, d, *J* = 8.1 Hz), 2.82 (1H, s), 1.96 (3H, s), 1.79 (3H, s); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 157.0, 142.3, 138.2, 131.0, 130.3, 129.8, 129.7,

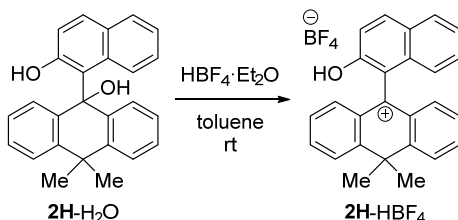
129.3, 128.6, 128.5, 127.6, 127.2, 121.9, 118.3, 116.0, 81.0, 37.9, 36.9, 31.7, one carbon atom was not found probably due to overlapping.; IR (film) 3150, 1617, 1595, 1506, 1486, 1456, 1384, 1228, 1051, 940, 911  $\text{cm}^{-1}$ ; HRMS (ESI) Calcd for  $\text{C}_{26}\text{H}_{20}\text{BrO}_2^-$  ( $[\text{M}-\text{H}]^-$ ) 443.0641 and 445.0621. Found 443.0648 and 445.0629.



**Preparation of 1-(10,10-dimethyl-9,10-dihydroanthracen-9-yl)-naphthalen-2-ol (2H-H<sub>2</sub>):** Cyclohexa-1,4-diene (1,4-CHD) (0.40 mL, 5.0 mmol) and trifluoroacetic acid (TFA) (0.23 mL, 2.0 mmol) were added to a solution of **2H-H<sub>2</sub>O** (366.5 mg, 1.0 mmol) in dichloromethane (10.0 mL) at room temperature. After overnight stirring, the reaction mixture was evaporated to afford the crude residue. Purification of the residue was conducted by column chromatography on silica gel (H/EA = 10:1 as eluent) to give **2H-H<sub>2</sub>** in quantitative yield (350.5 mg, 1.0 mmol) as a yellowish solid. **2H-H<sub>2</sub>**: <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN) *major rotamer*  $\delta$  7.81 (1H, d,  $J = 8.1$  Hz), 7.75 (1H, d,  $J = 8.1$  Hz), 7.71 (2H, d,  $J = 8.1$  Hz), 7.46 (1H, s), 7.38 (1H, d,  $J = 8.1$  Hz), 7.22 (2H, t,  $J = 8.1$  Hz), 7.08 (1H, dt,  $J = 1.8, 8.1$  Hz), 6.93 (2H, t,  $J = 8.1$  Hz), 6.91 (1H, d,  $J = 8.1$  Hz), 6.84 (1H, t,  $J = 8.1$  Hz), 6.66 (2H, d,  $J = 8.1$  Hz), 6.37 (1H, s), 2.04 (3H, s), 1.55 (3H, s); <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN) *major rotamer*  $\delta$  154.6, 143.9, 138.4, 132.9, 131.3, 130.1, 129.6, 128.3, 127.5, 126.9, 126.8<sub>0</sub>, 126.7<sub>5</sub>, 125.9, 123.5, 122.8, 118.6, 39.2, 39.1, 35.0, 29.6; IR (film) 1653, 1540, 1506, 1472, 1276, 1250, 808  $\text{cm}^{-1}$ ; HRMS (ESI) Calcd for  $\text{C}_{26}\text{H}_{21}\text{O}^-$  ( $[\text{M}-\text{H}]^-$ ) 349.1587. Found 349.1597.

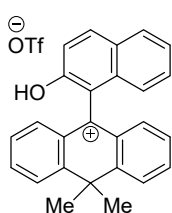


**2Br-H<sub>2</sub>**: The title compound was prepared as a yellowish solid from **2Br-H<sub>2</sub>O** by following the procedure for **2H-H<sub>2</sub>**. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN) *major rotamer*  $\delta$  7.95 (1H, d,  $J = 1.8$  Hz), 7.76 (1H, d,  $J = 8.1$  Hz), 7.71 (2H, d,  $J = 8.1$  Hz), 7.60 (1H, s), 7.41 (1H, d,  $J = 8.1$  Hz), 7.23 (2H, t,  $J = 8.1$  Hz), 6.94 (2H, t,  $J = 8.1$  Hz), 6.94 (1H, d,  $J = 8.1$  Hz), 6.80 (1H, d,  $J = 8.1$  Hz), 6.63 (2H, d,  $J = 8.1$  Hz), 6.34 (1H, s), 2.02 (3H, s), 1.54 (3H, s); <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN) *major rotamer*  $\delta$  155.1, 143.9, 138.1, 132.6, 131.6, 131.4, 129.4, 128.9, 128.8, 128.3, 127.6, 127.0, 126.8, 123.3, 119.8, 116.6, 39.2, 39.0, 34.8, 29.4; IR (film) 2966, 1700, 1654, 1636, 1540, 1506, 1457, 1360, 1253, 967  $\text{cm}^{-1}$ ; HRMS (ESI) Calcd for  $\text{C}_{26}\text{H}_{20}\text{BrO}^-$  ( $[\text{M}-\text{H}]^-$ ) 427.0692 and 429.0672. Found 427.0698 and 429.0678.

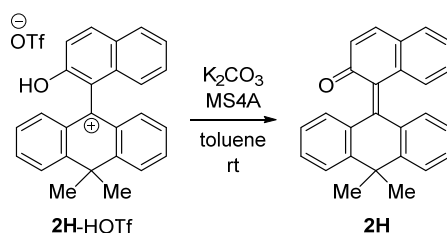


**Preparation of 9-(2-hydroxynaphthalen-1-yl)-10,10-dimethyl-9,10-dihydroanthracen-9-ylum tetrafluoroborate (2H-HBF<sub>4</sub>):** **2H-H<sub>2</sub>O** (18.3 mg, 0.05 mmol) was treated with tetrafluoroboric acid diethyl ether complex ( $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ ) (8.1 mg, 0.050 mmol) in toluene (1.0 mL) at room temperature for a few minutes to form deep-red precipitation. Precipitation was collected by filtration with toluene and dried under reduced pressure to

afford **2H**-HBF<sub>4</sub> in quantitative yield (21.8 mg, 0.050 mmol) as a deep-red solid. **2H**-HBF<sub>4</sub>: <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN) δ 8.40 (2H, d, *J* = 8.1 Hz), 8.35 (2H, t, *J* = 8.1 Hz), 8.22 (1H, d, *J* = 8.1 Hz), 8.02 (1H, d, *J* = 8.1 Hz), 7.94 (2H, d, *J* = 8.1 Hz), 7.92 (1H, brs), 7.61 (2H, t, *J* = 8.1 Hz), 7.45 (1H, d, *J* = 8.1 Hz), 7.44 (1H, t, *J* = 8.1 Hz), 7.35 (1H, t, *J* = 8.1 Hz), 6.98 (1H, d, *J* = 8.1 Hz), 2.03 (3H, s), 1.94 (3H, s); <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN) δ 197.7, 164.5, 153.0, 147.5, 141.4, 135.0<sub>1</sub>, 134.9<sub>7</sub>, 133.5, 131.2, 130.7, 129.5, 129.2, 128.9, 125.7, 125.5, 115.7, 46.1, 31.8, 31.2, one carbon atom was not found probably due to overlapping; <sup>19</sup>F NMR (376 MHz, CD<sub>3</sub>CN) δ -151.7 cm<sup>-1</sup>; IR (film) 3300, 2950, 1588, 1559, 1484, 1446, 1371, 1349, 1334, 1311, 1265, 1231, 1066, 978, 820 cm<sup>-1</sup>; HRMS (ESI) Calcd for C<sub>26</sub>H<sub>21</sub>O<sup>+</sup> ([M-BF<sub>4</sub>]<sup>+</sup>) 349.1587. Found 349.1588.



**2H**-HOTf: The title compound was prepared as a deep-red solid by following the above procedure using trifluoromethanesulfonic acid instead of HBF<sub>4</sub>·Et<sub>2</sub>O. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN) δ 8.39 (2H, d, *J* = 8.1 Hz), 8.34 (2H, t, *J* = 8.1 Hz), 8.22 (1H, d, *J* = 8.1 Hz), 8.12 (1H, br), 8.02 (1H, d, *J* = 8.1 Hz), 7.95 (2H, d, *J* = 8.1 Hz), 7.61 (2H, t, *J* = 8.1 Hz), 7.46 (1H, d, *J* = 8.1 Hz), 7.44 (1H, t, *J* = 8.1 Hz), 7.35 (1H, t, *J* = 8.1 Hz), 6.98 (1H, d, *J* = 8.1 Hz), 2.03 (3H, s), 1.94 (3H, s); <sup>13</sup>C NMR (151 MHz, CD<sub>3</sub>CN) δ 197.8, 164.4, 153.1, 147.5, 141.4, 135.0<sub>2</sub>, 134.9<sub>6</sub>, 133.5, 131.2, 130.7, 129.5, 129.2, 128.8, 125.7, 125.4, 115.7, 46.0, 31.8, 31.2, two carbon atom was not found probably due to overlapping or broadening.; <sup>19</sup>F NMR (376 MHz, CD<sub>3</sub>CN) δ -79.2, IR (film) 3164, 1590, 1564, 1482, 1448, 1373, 1343, 1284, 1228, 1173, 1028, 982, 818 cm<sup>-1</sup>; HRMS (ESI) Calcd for C<sub>26</sub>H<sub>21</sub>O<sup>+</sup> ([M-OTf]<sup>+</sup>) 349.1587. Found 349.1588.

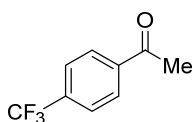


**Preparation of 1-(10,10-dimethylanthracen-9(10H)-ylidene)-naphthalen-2(1H)-one (2H):** In a glove box, a suspension of **2H**-HOTf (49.8 mg, 0.10 mmol), 4 Å molecular sieves (MS4A) (200.0 mg), and K<sub>2</sub>CO<sub>3</sub> (138.2 mg, 1.0 mmol) in toluene (10.0 mL) was stirred at room temperature overnight. The remaining solid was removed by filtration with toluene and the filtrate was concentrated to afford the crude residue. The resulting residue was dissolved in hexane and filtered for removing KOTf. Concentration of the filtrate furnished **2H** in quantitative yield (34.8 mg, 0.10 mmol) as a yellow solid. **2H**: <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.54 (1H, d, *J* = 7.8 Hz), 7.32 (1H, d, *J* = 7.8 Hz), 7.28 (1H, d, *J* = 7.8 Hz), 7.13 (1H, d, *J* = 7.8 Hz), 7.08 (1H, d, *J* = 7.8 Hz), 7.05 (1H, t, *J* = 7.8 Hz), 7.00 (1H, t, *J* = 7.8 Hz), 6.96 (1H, t, *J* = 7.6 Hz), 6.83 (1H, td, *J* = 1.8, 7.8 Hz), 6.80 (1H, t, *J* = 7.8 Hz), 6.79 (1H, d, *J* = 9.6 Hz), 6.67 (1H, t, *J* = 7.8 Hz), 6.56 (1H, dt, *J* = 1.8, 7.8 Hz), 6.28 (1H, d, *J* = 9.6 Hz), 1.64 (6H, s); <sup>13</sup>C NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>) δ 194.8, 149.0, 146.9, 146.2, 141.4, 138.1, 138.0, 135.1, 132.7, 131.0, 129.9, 128.8, 127.6, 126.8, 125.6, 125.3, 124.2, 123.8, 40.8, 28.0; IR (film) 2922, 1659, 1559, 1487, 1465, 1387, 1238, 1203, 830 cm<sup>-1</sup>; HRMS (ESI) Calcd for C<sub>26</sub>H<sub>21</sub>O<sup>+</sup> ([M+H]<sup>+</sup>) 349.1587. Found 349.1585.

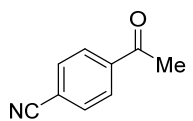
**Representative Procedure for 2Br-H<sub>2</sub>-catalyzed Oxidation of Benzylic Secondary Alcohols under Aerobic Photoirradiation Condition:**



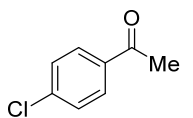
1-(4-Methylphenyl)ethanol (13.42 mg, 0.10 mmol), **2Br-H<sub>2</sub>** (2.15 mg, 0.0050 mmol), and dichloromethane (4.0 mL) were added to a test tube equipped with a stir bar. After bubbling with oxygen, the reaction mixture was irradiated with Kessil PR160L-456 Blue LED lamps with fans under oxygen atmosphere for 12 h. The reaction mixture was concentrated under reduced pressure. Purification of the residue was performed by column chromatography on Silica gel 60N (H/Et<sub>2</sub>O = 10:1 as eluent) to afford 4'-methylacetophenone in 99% yield (13.3 mg, 0.099 mmol). **4'-Methylacetophenone**<sup>1</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 (2H, t, *J* = 8.4 Hz), 7.25 (2H, d, *J* = 8.4 Hz), 2.57 (3H, s), 2.41 (3H, s); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.9, 144.0, 134.8, 129.3, 128.5, 26.6, 21.7.



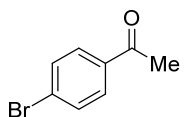
**4'-(Trifluoromethyl)acetophenone**<sup>2</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06 (2H, d, *J* = 8.0 Hz), 7.73 (2H, d, *J* = 8.0 Hz), 2.65 (3H, s); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.1, 139.8, 134.6 (q, *J*<sub>C-F</sub> = 32.8 Hz), 128.8, 125.8<sub>2</sub>, 125.8<sub>0</sub>, 123.7 (q, *J*<sub>C-F</sub> = 272.8 Hz), 26.9.



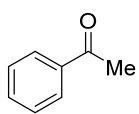
**4'-Cyanoacetophenone**<sup>3</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 (2H, td, *J* = 1.8, 8.6 Hz), 7.78 (2H, td, *J* = 1.8, 8.6 Hz), 2.65 (3H, s); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 196.7, 140.0, 132.6, 128.8, 118.0, 116.5, 26.9.



**4'-Chloroacetophenone**<sup>1</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (2H, td, *J* = 2.3, 8.4 Hz), 7.44 (2H, dt, *J* = 2.3, 8.4 Hz), 2.59 (3H, s); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.0, 139.7, 135.5, 129.8, 129.9, 26.7.



**4'-Bromoacetophenone**<sup>1</sup>: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.82 (2H, d, *J* = 8.5 Hz), 7.61 (2H, d, *J* = 8.5 Hz), 2.59 (3H, s); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.2, 135.9, 132.0, 130.0, 128.4, 26.7.

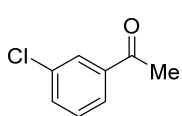


**Acetophenone**<sup>3</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (2H, td, *J* = 1.6, 7.2 Hz), 7.57 (1H, tt, *J* = 1.6, 7.2 Hz), 7.47 (2H, tt, *J* = 1.6, 7.2 Hz), 2.61 (3H, s); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 198.2, 137.2, 133.2, 128.7, 128.4, 26.7.

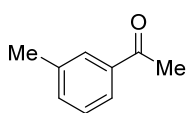
<sup>1</sup> S. Budweg, Z. Wei, H. Jiao, K. Junge, M. Beller, *ChemSusChem*, 2019, **12**, 2988.

<sup>2</sup> Q. Wang, H. Chai, Z. Yu, *Organometallics*, 2018, **37**, 584.

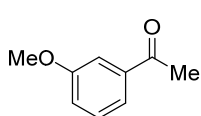
<sup>3</sup> M. J. Kim, Y. E. Jung, C. Y. Lee, J. Kim, *Tetrahedron Lett.*, 2018, **59**, 2722.



**3'-Chloroacetophenone**<sup>1</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (1H, t, *J* = 2.0 Hz), 7.83 (1H, td, *J* = 1.6, 7.8 Hz), 7.54 (1H, ddd, *J* = 1.6, 2.0, 7.8 Hz), 7.41 (1H, t, *J* = 7.8 Hz), 2.60 (3H, s); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 196.8, 138.7, 135.0, 133.1, 130.0, 128.5, 126.5, 26.7.

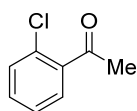


**3'-Methylacetophenone**<sup>2</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.78 (1H, s), 7.75 (1H, d, *J* = 7.6 Hz), 7.37 (1H, d, *J* = 7.6 Hz), 7.34 (1H, t, *J* = 7.6 Hz), 2.59 (3H, s), 2.41 (3H, s); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 198.5, 138.5, 137.3, 134.0, 128.9, 128.5, 125.7, 26.8, 21.4

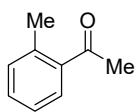


**3'-Methoxyacetophenone**<sup>4</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54 (1H, td, *J* = 1.4, 8.2 Hz), 7.49 (1H, dd, *J* = 1.4, 2.6 Hz), 7.37 (1H, t, *J* = 8.2 Hz), 7.11 (1H, ddd, *J* = 1.4, 2.6, 8.2 Hz), 3.86 (3H, s), 2.59 (3H, s); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 198.1, 159.9, 138.6, 129.7, 121.2, 119.7, 112.4,

55.5, 26.8.

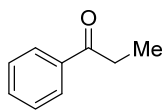


**2'-Chloroacetophenone**<sup>1</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 (1H, dd, *J* = 1.6, 8.0 Hz), 7.42 (1H, dd, *J* = 2.0, 8.0 Hz), 7.39 (1H, dt, *J* = 2.0, 8.0 Hz), 7.32 (1H, dt, *J* = 2.0, 8.0 Hz), 2.65 (3H, s); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 200.6, 139.2, 132.1, 131.4, 130.7, 129.5, 127.0, 30.8.



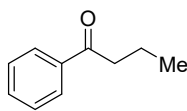
**2'-Methylacetophenone**<sup>2</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68 (1H, d, *J* = 7.8 Hz), 7.37 (1H, t, *J* = 7.8 Hz), 7.26 (1H, t, *J* = 7.8 Hz), 7.24 (1H, d, *J* = 7.8 Hz), 2.58 (3H, s), 2.53 (3H, s); <sup>13</sup>C NMR (151

MHz, CDCl<sub>3</sub>) δ 201.8, 138.5, 137.7, 132.1, 131.6, 129.4, 125.8, 29.6, 21.7.

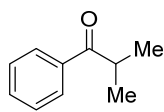


**Propiophenone**<sup>3</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (2H, td, *J* = 1.6, 7.2 Hz), 7.55 (1H, tt, *J* = 1.6, 7.2 Hz), 7.45 (2H, tt, *J* = 1.6, 7.2 Hz), 3.00 (2H, q, *J* = 7.2 Hz), 1.23 (3H, t, *J* = 7.2 Hz); <sup>13</sup>C

NMR (151 MHz, CDCl<sub>3</sub>) δ 200.9, 137.0, 132.9, 128.6, 128.0, 31.8, 8.3.



**Butyrophenone**<sup>3</sup>: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.96 (2H, d, *J* = 7.5 Hz), 7.56 (1H, t, *J* = 7.5 Hz), 7.46 (2H, t, *J* = 7.5 Hz), 2.95 (2H, t, *J* = 7.4 Hz), 1.77 (2H, sextet, *J* = 7.4 Hz), 1.01 (3H, t, *J* = 7.4 Hz); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 200.5, 137.2, 133.0, 128.6, 128.1, 40.6, 17.9, 14.0.

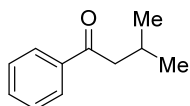


**Isobutyrophenone**<sup>5</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 (2H, d, *J* = 7.8 Hz), 7.55 (1H, tt, *J* = 2.0, 7.8 Hz), 7.46 (2H, t, *J* = 7.8 Hz), 3.56 (1H, septet, *J* = 6.8 Hz), 1.22 (6H, d, *J* = 6.8 Hz); <sup>13</sup>C NMR

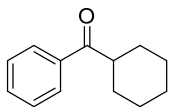
(151 MHz, CDCl<sub>3</sub>) δ 204.5, 136.3, 132.9, 128.7, 128.4, 35.4, 19.2.

<sup>4</sup> S. Muthaiah, S. H. Hong, *Adv. Synth. Catal.*, 2012, **354**, 3045.

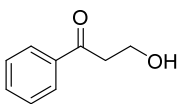
<sup>5</sup> C. Lei, D. Zhu, V. T. Tangcucoco III, J. S. Zhou, *Org. Lett.*, 2019, **21**, 5817.



**Isovalerophenone**<sup>5</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (2H, d, *J* = 7.5 Hz), 7.55 (1H, t, *J* = 7.5 Hz), 7.46 (2H, t, *J* = 7.5 Hz), 2.84 (2H, d, *J* = 6.6 Hz), 2.30 (1H, nonet, *J* = 6.6 Hz), 1.00 (6H, d, *J* = 6.6 Hz); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 200.4, 137.5, 133.0, 128.7, 128.2, 47.6, 25.3, 22.9.



**Cyclohexyl phenyl ketone**<sup>5</sup>: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.94 (2H, d, *J* = 7.5 Hz), 7.54 (1H, t, *J* = 7.5 Hz), 7.46 (2H, t, *J* = 7.5 Hz), 3.26 (1H, tt, *J* = 3.3, 11.3 Hz), 1.89 (2H, brd, *J* = 13.0 Hz), 1.85 (2H, td, *J* = 3.3, 13.0 Hz), 1.78-1.71 (1H, m), 1.50 (2H, dq, *J* = 3.3, 13.0 Hz), 1.39 (2H, tq, *J* = 3.3, 13.0 Hz), 1.27 (1H, tq, *J* = 3.3, 13.0 Hz); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 204.0, 136.5, 132.9, 128.7, 128.4, 45.8, 29.6, 26.1, 26.0.



**3-Hydroxypropiophenone**<sup>6</sup>: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.97 (2H, d, *J* = 7.2 Hz), 7.95 (1H, t, *J* = 7.2 Hz), 7.48 (2H, t, *J* = 7.2 Hz), 4.04 (2H, t, *J* = 5.4 Hz), 3.24 (2H, t, *J* = 5.4 Hz), 2.76 (1H, br); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 200.7, 136.8, 133.7, 128.8, 128.2, 58.2, 40.5.

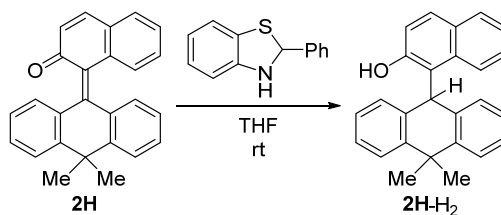
#### Procedure for Large Scale Oxidation of Benzylic Secondary Alcohol:



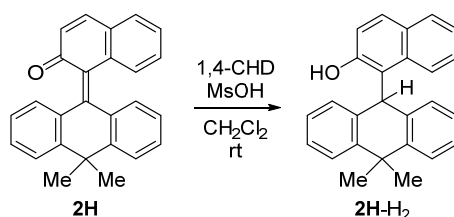
A solution of 1-(4-methylphenyl)ethanol (681.0 mg, 5.0 mmol), **2Br-H<sub>2</sub>** (107.3 mg, 0.25 mmol), in dichloromethane (200 mL) was placed in a 1-L 4-neck flask equipped with a condenser tube. After saturating the solution with oxygen by bubbling, the reaction mixture was stirred for 18 h under irradiation of Kessil PR160L-456 Blue LED lamps with fans under oxygen atmosphere. The reaction mixture was concentrated under reduced pressure to give a crude residue. Purification of the residue was performed by column chromatography on Silica gel 60N (H/Et<sub>2</sub>O = 10:1 as eluent) to afford 4'-methylacetophenone in 74% yield (497.8 mg, 3.71 mmol).

<sup>6</sup> C. Kuhakarn, K. Kittigowittana, M. Pohmakotr, V. Reutrakul, *Tetrahedron* 2005, **61**, 8995.

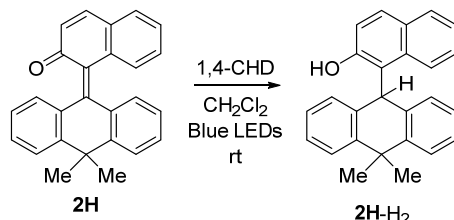
## Procedures for Reduction of **2H** and **2H-HBF<sub>4</sub>** with Organic Hydride Sources:



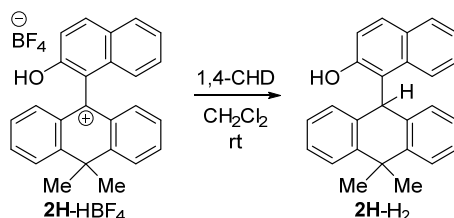
**2H** (3.48 mg, 0.010 mmol) was treated with 2-phenylbenzothiazoline (2.56 mg, 0.012 mmol) in THF (1.0 mL) at room temperature for 3 h. The reaction mixture was concentrated and the chemical yield of **2H-H<sub>2</sub>** was determined to be 40% by <sup>1</sup>H NMR analysis (400 MHz) using trimethylsilylbenzene as an internal standard.



To a solution of **2H** (3.48 mg, 0.010 mmol) and 1,4-CHD (4.7 μL, 0.050 mmol) in dichloromethane (1.0 mL) was added a 1.0 M solution of methanesulfonic acid in dichloromethane (1.0 μL, 0.0010 mmol), and the resulting solution was stirred at room temperature for 4 h. After concentration, the chemical yield of **2H-H<sub>2</sub>** was determined to be 64% by <sup>1</sup>H NMR analysis (400 MHz) using trimethylsilylbenzene as an internal standard.



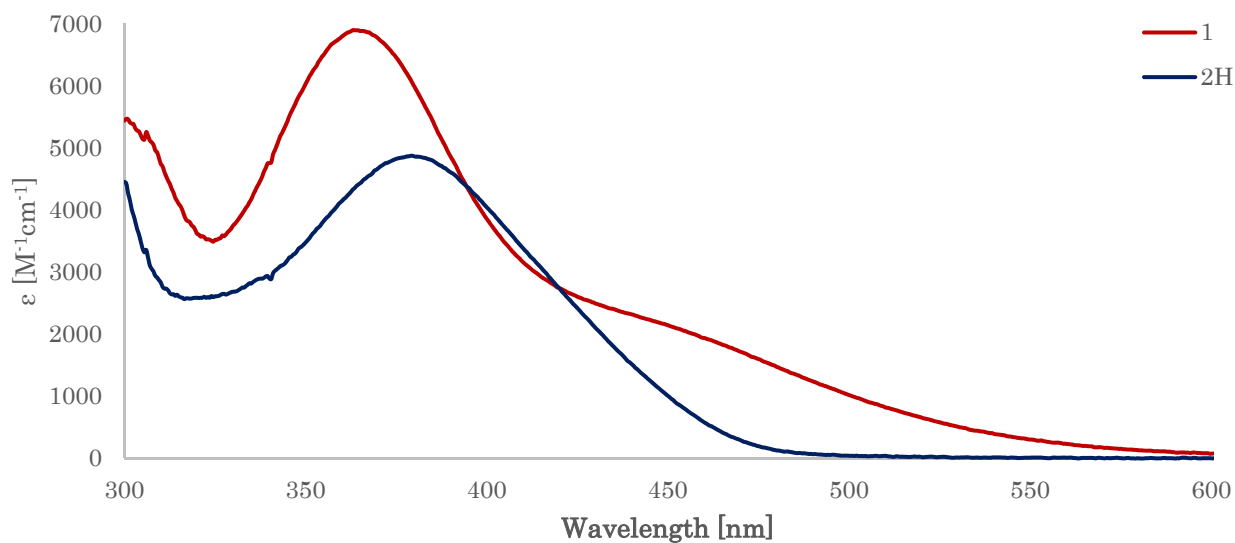
A solution of **2H** (3.48 mg, 0.010 mmol) and 1,4-CHD (4.7 μL, 0.050 mmol) in dichloromethane (1.0 mL) was irradiated with Kessil PR160L-456 Blue LED lamps with fans under argon atmosphere for 1 h. The reaction mixture was concentrated under reduced pressure for determining chemical yield of **2H-H<sub>2</sub>** to be 56% by <sup>1</sup>H NMR analysis (400 MHz) using trimethylsilylbenzene as an internal standard.



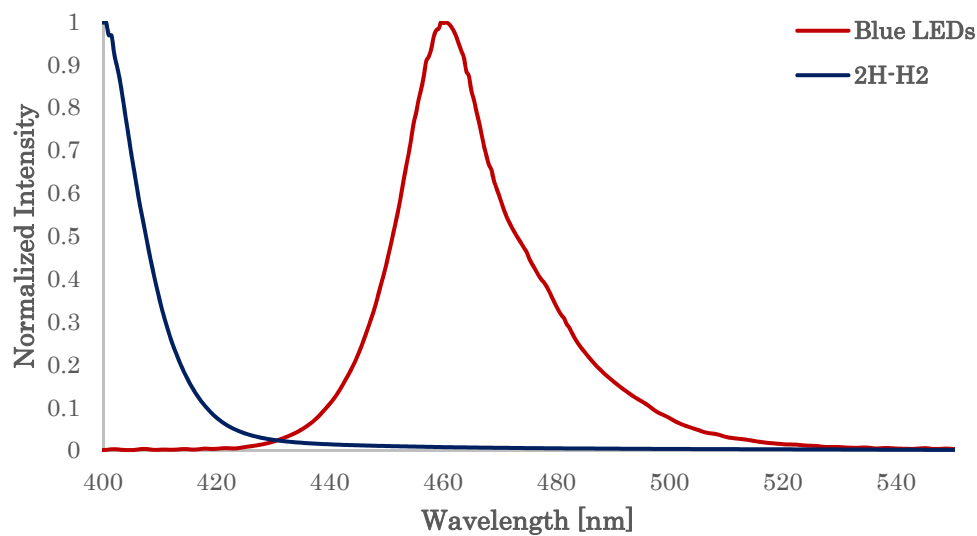
To a solution of **2H-HBF<sub>4</sub>** (4.36 mg, 0.010 mmol) in dichloromethane (1 mL) was added 1,4-CHD (4.7 μL, 0.050 mmol) at room temperature. After 4 h of stirring, the reaction mixture was concentrated and the <sup>1</sup>H NMR analysis of the crude residue using trimethylsilylbenzene as an internal standard determined the chemical yield of **2H-H<sub>2</sub>** to be 83%.



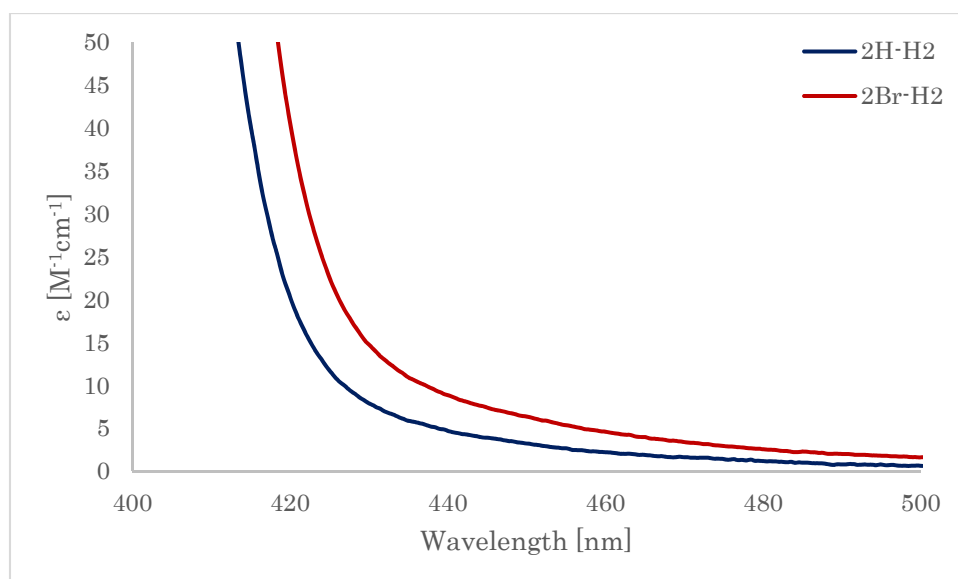
**Absorption Spectroscopy:** UV-Vis absorption spectra were recorded on a Shimadzu UV-1800 spectrometer.



**Figure S1.** Absorption spectra of **1** and **2H** in dichloromethane at room temperature.



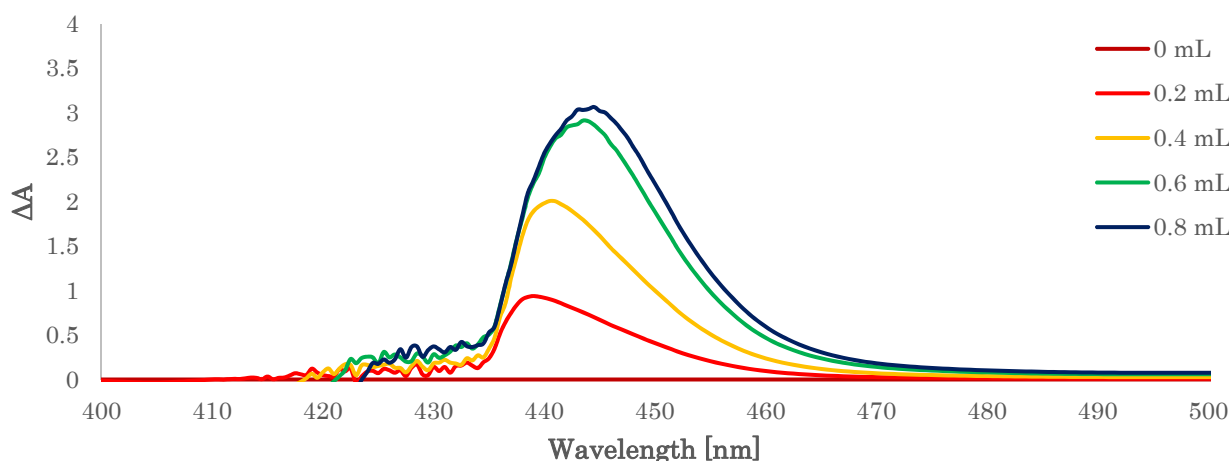
**Figure S2.** Absorption spectrum of **2H-H<sub>2</sub>** in dichloromethane and irradiation spectrum of Kessil PR160L-456 Blue LED lamp.



**Figure S3.** Absorption spectra of **2H-H<sub>2</sub>** and **2Br-H<sub>2</sub>** in dichloromethane at room temperature.

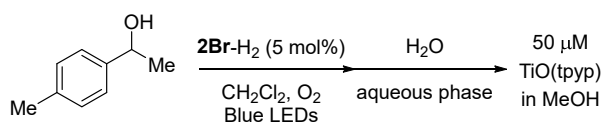
#### Detection of Hydrogen Peroxide:

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was detected upon treatment with oxo[5,10,15,20-tetra-(4-pyridyl)porphyrinato]titanium (IV) (TiO(tpyp)), which is known to rapidly react with even trace amounts of H<sub>2</sub>O<sub>2</sub>. To a 50 μM solution of TiO(tpyp) in MeOH (2.0 mL) was added 0~0.8 mL of a 30% aqueous solution of H<sub>2</sub>O<sub>2</sub>.<sup>7</sup> After being stirred for 5 min at room temperature, the mixture was analyzed by UV-Vis absorption spectroscopy measurement (*A*). A blank solution was prepared in a similar manner except for using distilled water instead of the sample solution and its absorbance was designated as *A<sub>B</sub>*. The difference in absorbance was determined as follows:  $\Delta A = A_B - A$ . An increasing peak at 442 nm suggests the generation of the Ti(O<sub>2</sub>)(tpyp) complex (Fig. S4).

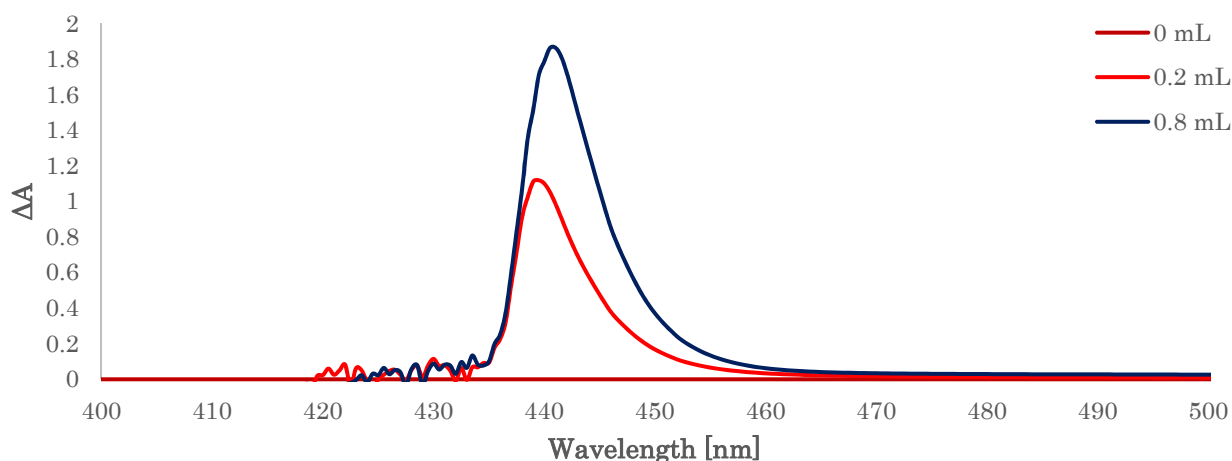


**Figure S4.** The difference in absorbance spectrum of the TiO(tpyp) in MeOH with a varied amount of 30% H<sub>2</sub>O<sub>2</sub> aq.

<sup>7</sup> (a) C. Matsubara, N. Kawamoto, K. Takamura, *Analyst*, 1992, **117**, 1781. (b) D. Uraguchi, M. Torii, T. Ooi, *ACS Catal.*, 2017, **7**, 2765.



A solution of phenethyl alcohol (13.42 mg, 0.10 mmol) and **2Br-H<sub>2</sub>** (2.15 mg, 0.0050 mmol) in dichloromethane (4.0 mL) in a test tube was irradiated with Kessil PR160L-456 Blue LED lamps with fans under oxygen atmosphere for 12 h. Distilled water (2.0 mL) was added to the reaction mixture, and the aqueous and organic phases were separated. The aqueous phase (0~0.8 mL) was introduced to a 50 μM solution of TiO(tpyp) in MeOH (2.0 mL). After being stirred for 5 min at room temperature, the solution was analyzed by UV-Vis absorption spectroscopy measurement.



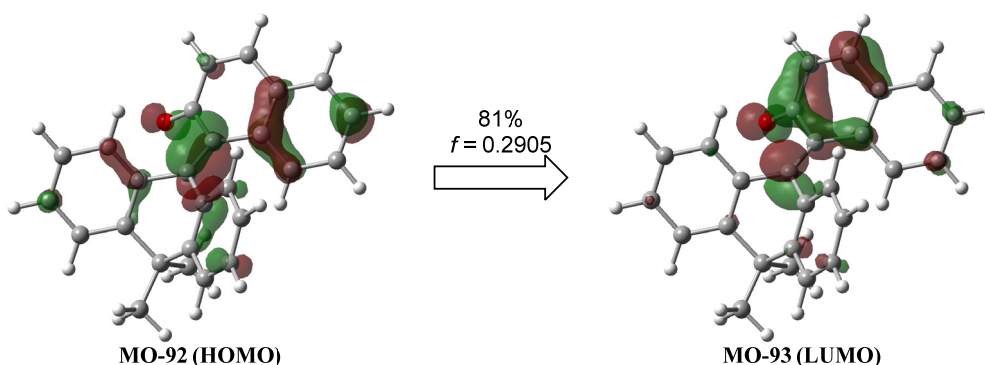
**Figure S5.** The difference in absorbance spectrum of the TiO(tpyp) in MeOH with a different amount of an aqueous phase of the reaction mixture.

### Computational Details:

**DFT Calculation:** The density functional theory (DFT) calculations were carried out using the Gaussian 09 Revision D.01 suite of programs<sup>8</sup> with default thresholds and algorithms unless otherwise noted. All stationary points were verified by the presence of all positive frequencies for local minima or a single negative frequency corresponding to the process of interest for transition states. Reported electronic energies do not include zero-point energy corrections.

**Photoexcitation from S<sub>0</sub> to S<sub>1</sub> States:** The first excited state of **2H** is reported below. Geometry optimizations were performed using DFT/time-dependent DFT (TD-DFT) with the CAM-B3LYP range-separated exchange correlation functional<sup>9</sup> employing the 6-31+G(d) basis set (CAM-B3LYP/6-31+G(d)). The dichloromethane solvent effects were taken into account by using the SMD model.<sup>10</sup>

Excited State	1:	Singlet-A	3.2802 eV	377.98 nm	f=0.2905	<S**2>=0.000
86 -> 93		0.10606	$(2 \times (0.10606)^2 = 0.02250)$		(2% contribution)	
87 -> 93		-0.17186	$(2 \times (0.17186)^2 = 0.05907)$		(6% contribution)	
89 -> 93		-0.11793	$(2 \times (0.11793)^2 = 0.02781)$		(3% contribution)	
90 -> 93		0.12732	$(2 \times (0.12732)^2 = 0.03242)$		(3% contribution)	
92 -> 93		0.63668	$(2 \times (0.63668)^2 = 0.81072)$		(81% contribution)	



**Figure S6.** The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **2H** at the geometry optimized in the S<sub>0</sub> state. The contribution (%) of the transition and oscillator strength (*f*) of the excitation is placed over the arrow.

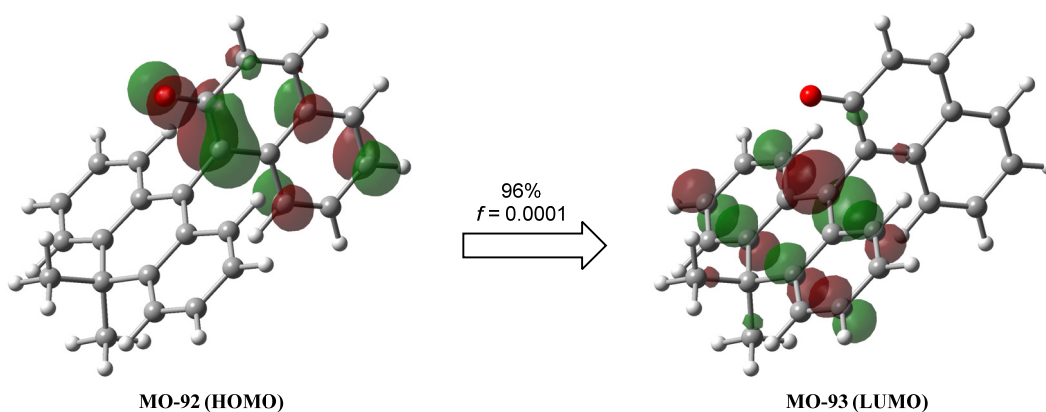
<sup>8</sup> Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

<sup>9</sup> T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51.

<sup>10</sup> A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378.

**Photoexcitation from  ${}^1S_0$  to  ${}^1S_1$  States:** The first excited state of  ${}^1S_0$  geometry of **2H** is reported below. Geometry optimizations in the  ${}^1S_1$  state were performed at the TD-CAMB3LYP/6-31+G(d) level of theory with QC-SCF method.<sup>11</sup> The dichloromethane solvent effects were taken into account by using the SMD model.

Excited State 1: Singlet-A 0.5826 eV 2128.27 nm  $f=0.0001$   $\langle S^2 \rangle=0.000$   
 92 -> 93 0.69367  $(2 \times (0.69367)^2 = 0.96236$  (96% contribution)



**Figure S7.** The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **2H** at the geometry optimized in the  ${}^1S_0$  state. The contribution (%) of the transition and oscillator strength ( $f$ ) of the excitation is placed over the arrow.

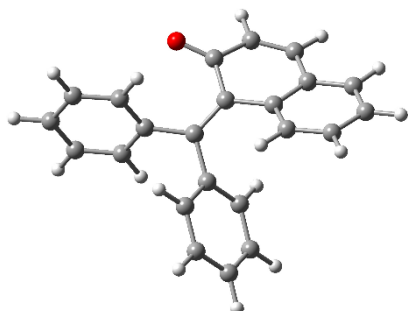
**Estimating Triplet Energy of 2H-H<sub>2</sub>:** Triplet energy of **2H-H<sub>2</sub>** was estimated through calculation of energy difference between ground-state and excited-state energies at the  $T_0$  geometry of **2H-H<sub>2</sub>**. Geometry optimization was performed at the UCAMB3LYP/6-31+G(d) level of theory. The dichloromethane solvent effects were taken into account by using the SMD model.

$$E(S^T_0) = -1078.69522705 \text{ a.u.} \quad E(T_0) = -1078.61546284 \text{ a.u.}$$

$$\Delta E(T_0 - S^T_0) = 0.07976421 \text{ a.u.} = 2.17 \text{ eV}$$

#### Cartesian Coordinates of Calculated Structures

1  $E = -960.807292395$  a.u.



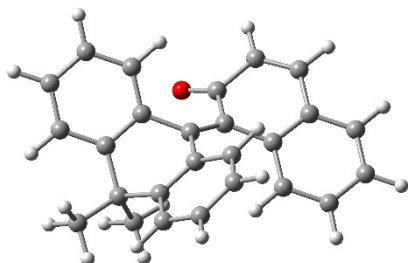
C -0.429345 -0.927309 0.139863

C	-0.186246	-2.364114	-0.211571
C	-1.269248	-3.021248	-0.957906
C	-2.513672	-2.515601	-0.987566
C	-2.865971	-1.302071	-0.268169
C	-4.208695	-0.936720	-0.112568
C	-4.559096	0.155617	0.667067
C	-3.558447	0.879615	1.317019
C	-2.222407	0.536738	1.151641
C	-1.846364	-0.533901	0.330984
O	0.855705	-2.972768	0.019186
H	-1.021510	-3.970214	-1.424126
H	-3.310668	-3.046750	-1.502955

<sup>11</sup> Bacskay, G. B. *Chem. Phys.* **1981**, *61*, 385–404.

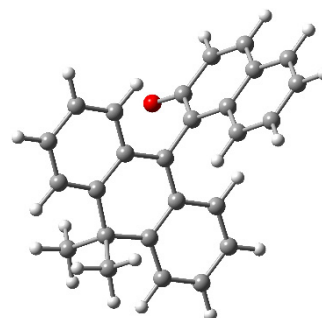
H	-4.975840	-1.535315	-0.597015	C	4.725094	-0.023810	-0.019999
H	-5.602894	0.429785	0.788049	H	5.639817	-0.529928	-0.317670
H	-3.820353	1.715115	1.959835	C	-0.997108	3.753758	-1.198959
H	-1.462108	1.104294	1.675785	H	-1.232610	4.787779	-1.435052
C	0.600914	-0.033316	0.068386	C	-3.793220	1.535027	1.161534
C	0.384992	1.432048	-0.120749	H	-4.348812	1.704341	0.233467
C	-0.420814	1.904438	-1.163022	H	-3.661153	2.497580	1.663232
C	-0.578532	3.270319	-1.373149	H	-4.408661	0.919639	1.823432
C	0.058476	4.185864	-0.537886	C	3.512455	-0.717014	-0.092479
C	0.870456	3.725689	0.496871	C	4.767707	1.278924	0.458204
C	1.045621	2.359426	0.693048	H	5.714334	1.807242	0.521934
C	2.041583	-0.412855	0.094417	C	-1.805010	3.050074	-0.308078
C	2.880429	-0.049753	-0.965400	H	-2.662357	3.552028	0.125425
C	4.241375	-0.336347	-0.922528	C	-1.757839	0.693676	2.297974
C	4.789581	-0.951217	0.201096	H	-2.386180	0.075055	2.947614
C	3.966529	-1.291252	1.273147	H	-1.624398	1.669687	2.777038
C	2.600791	-1.034690	1.214896	H	-0.778823	0.214657	2.223695
H	-0.920448	1.196534	-1.817259	C	2.418999	-2.903397	-0.228380
H	-1.200483	3.619458	-2.192579	H	2.432750	-3.979306	-0.375395
H	-0.069437	5.252543	-0.698829	C	-2.773232	-2.914578	-1.190568
H	1.376566	4.432103	1.148794	H	-2.848929	-3.833440	-1.764814
H	1.690178	2.008481	1.493778	C	-2.435902	0.868479	0.917659
H	2.461856	0.451130	-1.833905	C	-3.896086	-2.373975	-0.571250
H	4.875390	-0.067551	-1.762740	H	-4.857968	-2.873108	-0.648890
H	5.854517	-1.162210	0.242646	C	3.496959	-2.131982	-0.448803
H	4.387594	-1.767045	2.154398	H	4.422737	-2.569797	-0.814765
H	1.960535	-1.314369	2.045111	C	3.589043	1.888202	0.886724
				H	3.613845	2.890972	1.303398

**2H** ( $S_0$ )  $E = -1077.48159482$  a.u.



O	0.396758	-3.000105	0.972543
C	-1.540025	1.715873	0.004143
C	-0.406610	1.109223	-0.565721
C	-2.579614	-0.498177	0.231978
C	1.200990	-2.316116	0.350487
C	-3.797176	-1.172634	0.125990
H	-4.692917	-0.754377	0.569997
C	2.306099	-0.074715	0.261794
C	-0.163225	-0.319784	-0.230838
C	-1.550031	-2.267217	-1.074848
H	-0.675601	-2.680954	-1.566765
C	-1.436958	-1.085262	-0.341499
C	1.039024	-0.840630	0.128201
C	2.373973	1.218953	0.787996
H	1.471233	1.708334	1.133816
C	0.379234	1.805711	-1.485774
H	1.221861	1.307983	-1.955069
C	0.086985	3.125890	-1.805392
H	0.700609	3.659461	-2.525537

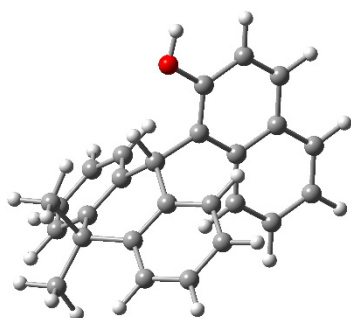
**2H** ( $S_0$ )  $E = -1077.45494301$  a.u.



C	1.302184	0.012919	0.689991
C	1.662225	0.024830	2.062434
C	3.090357	0.028100	2.361161
C	4.049267	0.018276	1.402467
C	3.700253	0.006060	0.015138
C	4.658074	-0.006754	-1.008915
C	4.302846	-0.018519	-2.374476
C	2.952755	-0.017645	-2.736669
C	1.980596	-0.006002	-1.764459
C	2.323111	0.005127	-0.333316
O	0.811336	0.032273	3.006780
H	3.361862	0.037358	3.413578
H	5.103190	0.019657	1.669726
H	5.710052	-0.007351	-0.737968
H	5.081486	-0.027668	-3.128700
H	2.667659	-0.025720	-3.783286

H	0.932617	-0.004983	-2.038485
C	-0.115865	0.005056	0.290372
C	-0.828584	1.244730	0.126313
C	-0.135407	2.477056	0.225336
C	-0.784281	3.690840	0.087453
C	-2.153477	3.708426	-0.168149
C	-2.847296	2.503213	-0.281739
C	-2.216812	1.266092	-0.143690
C	-3.044970	-0.010823	-0.285102
C	-2.205435	-1.278907	-0.131530
C	-2.824536	-2.522892	-0.259029
C	-2.120181	-3.720796	-0.132859
C	-0.751689	-3.688519	0.124864
C	-0.113830	-2.467677	0.251497
C	-0.817724	-1.242407	0.139813
C	-3.710724	-0.020308	-1.681324
C	-4.146531	-0.010811	0.799203
H	0.934167	2.454879	0.411099
H	-0.226980	4.618831	0.177369
H	-2.683877	4.649525	-0.278802
H	-3.912924	2.540833	-0.483137
H	-3.889436	-2.572133	-0.461805
H	-2.641950	-4.667575	-0.235853
H	-0.186177	-4.610566	0.224168
H	0.955510	-2.434430	0.437038
H	-4.339183	-0.906226	-1.809326
H	-2.956097	-0.020350	-2.474778
H	-4.347655	0.858370	-1.817371
H	-3.708009	-0.003220	1.802026
H	-4.780757	-0.897872	0.710441
H	-4.790155	0.868476	0.701114

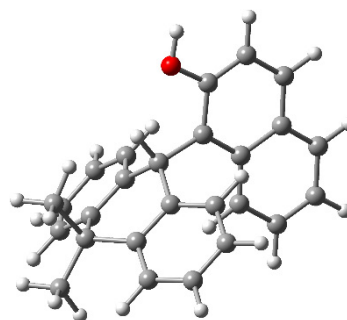
**2H-H<sub>2</sub> (S<sub>0</sub>)**  $E = -1078.71412258$  a.u.



C	3.494146	-0.000009	1.587143
H	4.103910	-0.887938	1.787135
H	2.658391	-0.000063	2.292619
H	4.103787	0.888006	1.787125
C	-1.505799	-0.000047	-1.626252
H	-0.426943	-0.000068	-1.719991
C	0.200768	0.000020	0.871707
H	0.490711	0.000044	1.928322
C	-1.320550	0.000048	0.871549
C	2.713542	2.426094	-0.651557
H	3.745141	2.445448	-0.981752
C	0.821383	-1.262840	0.279859
C	2.168305	1.253076	-0.117770

C	1.963719	3.592498	-0.768927
H	2.417683	4.485912	-1.188966
C	0.081348	-2.442575	0.175444
H	-0.955241	-2.450618	0.495950
C	1.963506	-3.592629	-0.768767
H	2.417406	-4.486088	-1.188778
C	0.081471	2.442598	0.175310
H	-0.955120	2.450721	0.495806
C	0.821434	1.262823	0.279792
C	4.284164	0.000000	-0.762286
H	4.050540	-0.000459	-1.832270
H	4.904644	-0.872511	-0.545188
H	4.904089	0.873072	-0.545829
C	0.640747	-3.605229	-0.342532
H	0.042675	-4.509110	-0.418382
C	2.168257	-1.253181	-0.117714
C	3.022188	-0.510000	0.110416
O	-1.260035	0.000123	3.234793
H	-1.852914	0.000221	4.004777
C	2.713402	-2.426265	-0.651466
H	3.744981	-2.445716	-0.981696
C	0.640951	3.605193	-0.342715
H	0.042936	4.509107	-0.418616
C	-1.990311	0.000105	2.077345
C	-2.098635	0.150000	-0.332721
C	-3.405495	0.000139	2.153399
H	-3.884434	0.000183	3.129710
C	-3.521860	0.000046	-0.261993
C	-2.274127	-0.000080	-2.764241
H	-1.790687	-0.000128	-3.737251
C	-4.291010	0.000011	-1.454782
H	-5.375057	0.000032	-1.370801
C	-4.151074	0.000110	1.009997
H	-5.236488	0.000136	1.062599
C	-3.685317	-0.000052	-2.684835
H	-4.280649	-0.000081	-3.593284

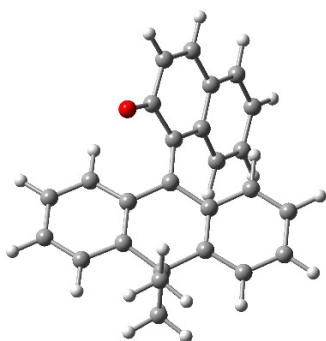
**2H-H<sub>2</sub> (T<sub>0</sub>)**  $E = -1078.61546284$  a.u.



C	3.494362	-0.000114	1.582414
H	4.104264	-0.888060	1.781706
H	2.658973	-0.000362	2.288445
H	4.104025	0.887919	1.782047
C	-1.511405	0.000363	-1.621900
H	-0.433091	0.000379	-1.720131
C	0.196198	-0.000209	0.866100
H	0.483391	-0.000382	1.922950
C	-1.316851	-0.000291	0.851195

C	2.713244	2.428411	-0.650089
H	3.744930	2.448316	-0.979940
C	0.820890	-1.264246	0.275116
C	2.167444	1.253572	-0.120350
C	1.964222	3.595579	-0.763500
H	2.419027	4.490053	-1.180285
C	0.081149	-2.444569	0.174828
H	-0.956231	-2.452448	0.493732
C	1.964620	-3.595223	-0.764772
H	2.419519	-4.489501	-1.181876
C	0.080868	2.444390	0.175696
H	-0.956511	2.452049	0.494607
C	0.820733	1.264109	0.275557
C	4.282021	0.000415	-0.768284
H	4.047015	0.000248	-1.837948
H	4.902757	-0.872094	-0.552078
H	4.902189	0.873371	-0.552233
C	0.641669	-3.608348	-0.338705
H	0.044687	-4.513129	-0.411601
C	2.167602	-1.253413	-0.120797
C	3.021162	0.000103	0.106055
O	-1.226672	-0.001022	3.234067
H	-1.764395	-0.001269	4.046117
C	2.713518	-2.428015	-0.650953
H	3.745198	-2.447713	-0.980821
C	0.641269	3.608412	-0.337425
H	0.044194	4.513158	-0.409992
C	-2.034152	-0.000671	2.142243
C	-2.093959	0.000015	-0.353124
C	-3.387301	-0.000656	2.216824
H	-3.886499	-0.000937	3.182179
C	-3.540357	0.000023	-0.268007
C	-2.297821	0.000706	-2.812486
H	-1.797966	0.000985	-3.776330
C	-4.287088	0.000355	-1.443406
H	-5.371917	0.000361	-1.377690
C	-4.160922	-0.000298	1.012567
H	-5.244734	-0.000293	1.072493
C	-3.660802	0.000695	-2.724322
H	-4.277337	0.000962	-3.618736

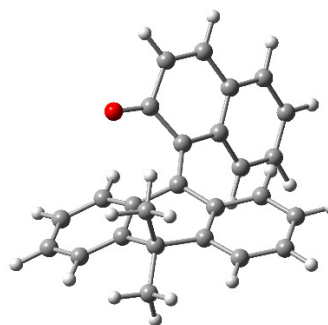
**2H-Int1** ( $S_0$ )  $E = -1077.46848133$  a.u.



C	-1.209378	0.689706	-0.323877
C	-1.462160	1.759479	-1.301396
C	-2.861349	1.981861	-1.671141

C	-3.884354	1.308419	-1.110194
C	-3.667873	0.336001	-0.067826
C	-4.758281	-0.262318	0.587616
C	-4.565057	-1.128985	1.646280
C	-3.257822	-1.383986	2.085589
C	-2.176185	-0.802897	1.451195
C	-2.341740	0.037365	0.326785
O	-0.574081	2.388027	-1.911471
H	-3.029101	2.733916	-2.436712
H	-4.909038	1.510746	-1.414822
H	-5.763548	-0.016874	0.253714
H	-5.413143	-1.585752	2.147610
H	-3.089656	-2.031973	2.941444
H	-1.178884	-0.995226	1.833000
C	0.127271	0.243296	-0.143338
C	1.177759	1.190636	0.203111
C	0.824893	2.503739	0.592995
C	1.774988	3.435053	0.947646
C	3.122828	3.065370	0.951405
C	3.482172	1.762426	0.649814
C	2.528682	0.798432	0.298205
C	2.986728	-0.634336	0.097002
C	1.838949	-1.582515	-0.208067
C	2.143398	-2.932078	-0.434062
C	1.179640	-3.843351	-0.828475
C	-0.129993	-3.410481	-1.050827
C	-0.451303	-2.089780	-0.826217
C	0.500437	-1.159490	-0.345129
C	3.702376	-1.107955	1.386547
C	3.985413	-0.679696	-1.086769
H	-0.220912	2.777752	0.625726
H	1.476628	4.438896	1.233751
H	3.888655	3.786229	1.223478
H	4.529727	1.487773	0.703896
H	3.165039	-3.276157	-0.316780
H	1.452368	-4.881392	-0.995884
H	-0.886184	-4.099741	-1.413869
H	-1.458386	-1.758118	-1.037748
H	4.049667	-2.138611	1.279597
H	3.028273	-1.061324	2.247765
H	4.575450	-0.487258	1.601754
H	3.503451	-0.363631	-2.017255
H	4.377626	-1.689812	-1.229300
H	4.834377	-0.017154	-0.898826

**2H-TS1** ( $S_0$ )  $E = -1077.46639587$  a.u.

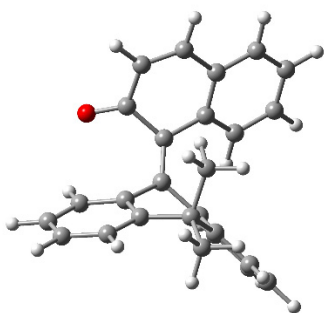


C	-1.147230	-0.662202	0.233534
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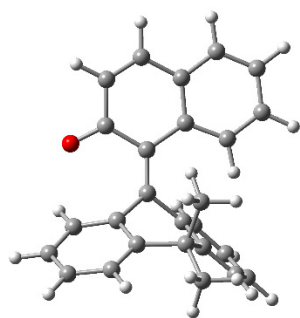


C	-1.208211	-1.772352	1.221741	C	0.935106	-0.936276	-0.654821
C	-2.478600	-1.894049	1.953366	C	0.854929	-2.420857	-0.455252
C	-3.594131	-1.227919	1.606929	C	1.547410	-2.936847	0.731783
C	-3.623204	-0.362098	0.448451	C	2.556005	-2.236804	1.274713
C	-4.838467	0.136284	-0.044045	C	3.019470	-0.984293	0.690935
C	-4.885163	0.851012	-1.229289	C	4.240196	-0.445374	1.105675
C	-3.704146	1.052060	-1.952526	C	4.774371	0.674125	0.481224
C	-2.497328	0.574422	-1.469138	C	4.087399	1.243476	-0.585967
C	-2.414866	-0.099631	-0.234994	C	2.857848	0.728933	-0.991761
O	-0.260968	-2.494716	1.562491	C	2.276158	-0.363597	-0.344411
H	-2.469359	-2.594001	2.783741	O	0.240964	-3.172550	-1.204677
H	-4.518838	-1.374901	2.160544	H	1.264593	-3.924979	1.082049
H	-5.751166	-0.069765	0.509582	H	3.114788	-2.634987	2.118278
H	-5.831351	1.227355	-1.606536	H	4.779206	-0.931638	1.914554
H	-3.730858	1.574915	-2.904384	H	5.727690	1.080268	0.805861
H	-1.595107	0.719348	-2.055360	H	4.509155	2.091651	-1.117522
C	0.123048	-0.148988	-0.076855	H	2.371602	1.172690	-1.845782
C	1.184970	-1.088261	-0.434647	C	-0.226975	-0.225866	-0.750418
C	0.816852	-2.293722	-1.064657	C	-0.340012	1.259043	-0.686938
C	1.763852	-3.200143	-1.499110	C	0.135079	2.103451	-1.689959
C	3.114266	-2.905678	-1.317698	C	-0.046035	3.481080	-1.605005
C	3.494737	-1.700266	-0.741014	C	-0.715845	4.015635	-0.512128
C	2.548442	-0.763818	-0.314343	C	-1.256232	3.169870	0.456303
C	2.961529	0.554839	0.315639	C	-1.109742	1.786319	0.369012
C	1.873628	1.615881	0.126155	C	-1.810712	0.804438	1.318245
C	2.219045	2.967503	0.250245	C	-2.384385	-0.310071	0.425201
C	1.268410	3.976418	0.260949	C	-3.669145	-0.823642	0.593911
C	-0.081516	3.643060	0.195015	C	-4.187483	-1.776683	-0.282867
C	-0.447075	2.315363	0.080140	C	-3.425809	-2.220912	-1.355495
C	0.503863	1.279120	-0.007573	C	-2.129704	-1.741182	-1.525410
C	4.321066	1.025715	-0.230769	C	-1.593141	-0.816077	-0.629566
C	3.115036	0.326867	1.844289	C	-2.906237	1.495574	2.137173
H	-0.235525	-2.499236	-1.223269	C	-0.799698	0.216194	2.331309
H	1.457724	-4.123598	-1.981228	H	0.612622	1.679500	-2.566324
H	3.876899	-3.604909	-1.649127	H	0.328658	4.126733	-2.393963
H	4.552527	-1.494078	-0.637222	H	-0.854993	5.089577	-0.425466
H	3.258265	3.250124	0.357023	H	-1.822676	3.608492	1.269363
H	1.580374	5.013519	0.344840	H	-4.295911	-0.470316	1.404367
H	-0.847478	4.411456	0.241410	H	-5.196803	-2.150336	-0.134012
H	-1.500051	2.083184	0.057219	H	-3.832098	-2.939730	-2.061302
H	4.656936	1.934278	0.270839	H	-1.531111	-2.081578	-2.359507
H	4.282962	1.218407	-1.307940	H	-3.383194	0.783052	2.815455
H	5.093953	0.278738	-0.042388	H	-3.680847	1.942941	1.506298
H	2.176705	-0.013624	2.291972	H	-2.475639	2.281666	2.763220
H	3.417353	1.256404	2.337550	H	0.035428	-0.293306	1.847864
H	3.880945	-0.432399	2.034035	H	-1.303442	-0.504620	2.984319
				H	-0.391657	1.017363	2.956766

**2H-Int2** ( $S_0$ )  $E = -1077.47299015$  a.u.



**2H-TS2** ( $S_0$ )  $E = -1077.46760971$  a.u.



C	1.051738	-0.909440	-0.360289
C	1.267728	-2.393339	-0.396765
C	2.514772	-2.955410	0.109714
C	3.569234	-2.170942	0.362532
C	3.482704	-0.726293	0.290868
C	4.631769	0.003651	0.625588
C	4.610072	1.384114	0.707225
C	3.400689	2.035154	0.482849
C	2.259080	1.321225	0.140574
C	2.257116	-0.077202	-0.017803
O	0.461835	-3.162397	-0.924131
H	2.567230	-4.038386	0.157931
H	4.525207	-2.602163	0.649366
H	5.544743	-0.545123	0.841781
H	5.506533	1.940577	0.963579
H	3.333455	3.115254	0.577106
H	1.359117	1.893688	0.003013
C	-0.220332	-0.409341	-0.541123

C	-0.514443	1.023046	-0.802961
C	-0.034655	1.649970	-1.954295
C	-0.379428	2.968639	-2.225173
C	-1.199624	3.658871	-1.336601
C	-1.707372	3.020165	-0.205681
C	-1.395275	1.687803	0.062430
C	-1.986799	0.873223	1.216302
C	-2.398497	-0.470011	0.586659
C	-3.632550	-1.056264	0.861054
C	-4.068466	-2.187860	0.174188
C	-3.273592	-2.732309	-0.823759
C	-2.015534	-2.193043	-1.078483
C	-1.538073	-1.102365	-0.347468
C	-3.171282	1.596660	1.864895
C	-0.930366	0.655615	2.325575
H	0.619022	1.102815	-2.627585
H	-0.006561	3.455041	-3.121772
H	-1.466786	4.693429	-1.532818
H	-2.371489	3.570002	0.451542
H	-4.290559	-0.612109	1.598282
H	-5.042444	-2.613466	0.399310
H	-3.620660	-3.580022	-1.407558
H	-1.403615	-2.618507	-1.857151
H	-3.569697	1.013540	2.699391
H	-3.984796	1.787260	1.157853
H	-2.845850	2.555313	2.278830
H	-0.032824	0.152684	1.961551
H	-1.356343	0.044656	3.128551
H	-0.630049	1.618806	2.751537

**Crystallographic Structure Determination of 1:** The single crystal, obtained by the procedure described below, was mounted on MicroMesh. Data of X-ray diffraction were collected at 123 K on a Rigaku FR-X with Pilatus 200K with fine-focus sealed tube Mo/K $\alpha$  radiation ( $\lambda = 0.71075 \text{ \AA}$ ). An absorption correction was made using Crystal Structure. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on  $F^2$  by using SHELXL-2014.<sup>12</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and their isotropic thermal parameters were refined.

**Recrystallization of 1:** Recrystallization of **1** was performed by using a CH<sub>2</sub>Cl<sub>2</sub>/hexane solvent system at room temperature.

**Crystallographic Structure Determination of 2H:** The single crystal, obtained by the procedure described below, was mounted on MicroMesh. Data of X-ray diffraction were collected at 123 K on a Rigaku FR-X with Pilatus 200K with fine-focus sealed tube Mo/K $\alpha$  radiation ( $\lambda = 0.71075 \text{ \AA}$ ). An absorption correction was made using Crystal Structure. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on  $F^2$  by using SHELXL-2014.<sup>10</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and their isotropic thermal parameters were refined.

**Recrystallization of 2H:** Recrystallization of **2H** was performed by using a Et<sub>2</sub>O/hexane solvent system at room temperature in a glove box.

**Crystallographic Structure Determination of 2H-HBF<sub>4</sub>:** The single crystal, which was obtained by the procedure described below, was mounted on MicroMesh. Data of X-ray diffraction were collected at 123 K on a Rigaku MicroMax-007HF with R-Axis RAPID II with fine-focus sealed tube Cu/K $\alpha$  radiation ( $\lambda = 1.54187 \text{ \AA}$ ). An absorption correction was made using RAPID-AUTO. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on  $F^2$  by using SHELXL-2014.<sup>10</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. A hydrogen atom bonded to the oxygen atom was located from a difference synthesis and its coordinates and isotropic thermal parameters were refined. The other hydrogen atoms were placed in calculated positions and isotropic thermal parameters were refined.

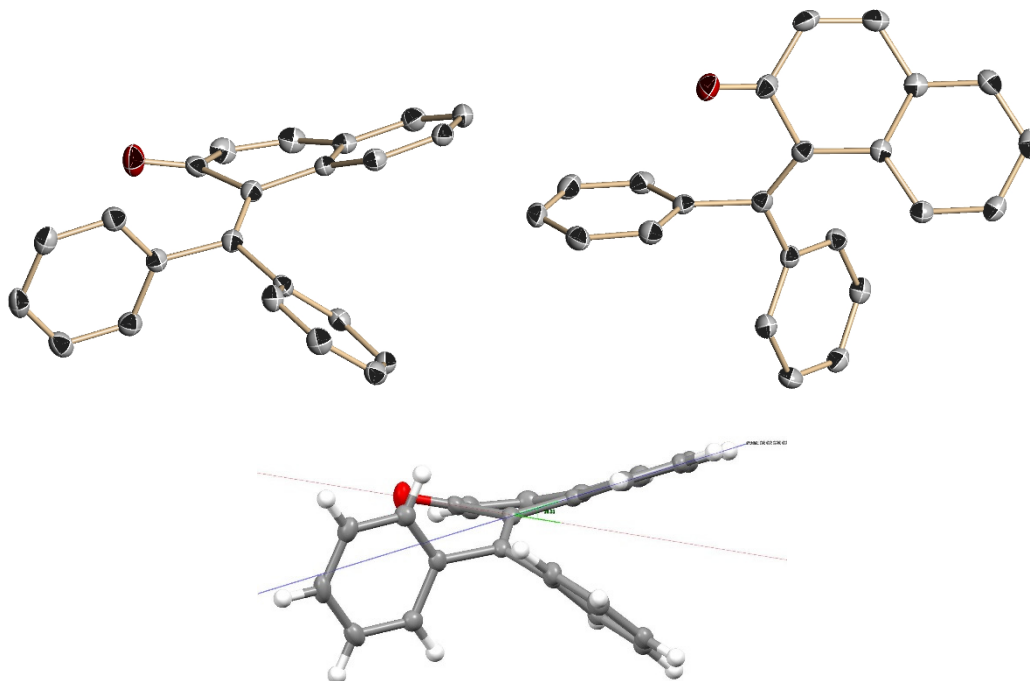
**Recrystallization of 2H-HBF<sub>4</sub>:** Recrystallization of **2H-HBF<sub>4</sub>** was performed by using a CH<sub>2</sub>Cl<sub>2</sub>/hexane solvent system at room temperature.

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<sup>12</sup> G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.

**Table S1.** Crystal data and structure refinement for quinone methide **1** (CCDC-1993085).

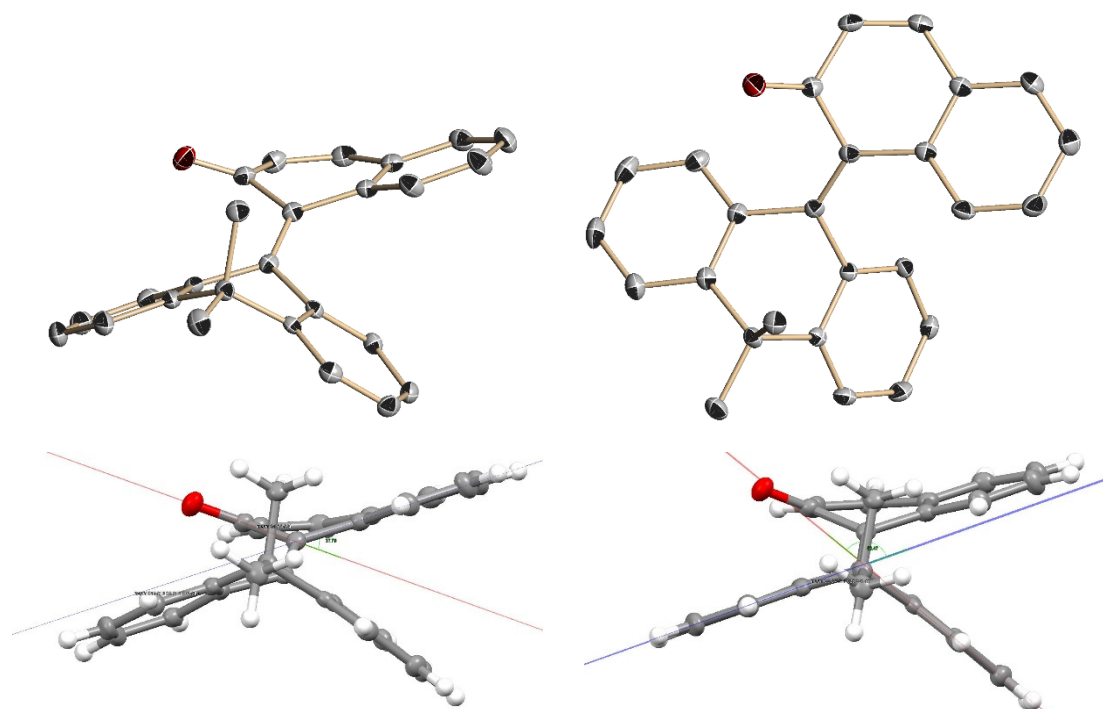
Empirical formula	C <sub>26</sub> H <sub>20</sub> O <sub>1</sub>	
Formula weight	348.42	
Temperature	123(2) K	
Wavelength	0.71075 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.294(3) Å	$\alpha = 90^\circ$
	b = 16.632(4) Å	$\beta = 112.274(2)$
	c = 11.319(3) Å	$\gamma = 90^\circ$
Volume	1793.3(8) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.290 Mg/m <sup>3</sup>	
Absorption coefficient	0.079 mm <sup>-1</sup>	
F(000)	648	
Crystal size	0.10 x 0.070 x 0.060 mm <sup>3</sup>	
Theta range for data collection	3.0 to 27.5°	
Index ranges	-11 ≤ h ≤ 9, -12 ≤ k ≤ 12, -14 ≤ l ≤ 20	
Reflections collected	11456	
Independent reflections	2875 [R <sub>int</sub> = 0.0248]	
Completeness to theta = 25.242°	98.7%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.948 and 1.000	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	2875 / 0 / 217	
Goodness-of-fit on F <sup>2</sup>	1.074	
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0354, wR <sub>2</sub> = 0.0765	
R indices (all data)	R <sub>1</sub> = 0.0487, wR <sub>2</sub> = 0.0836	
Largest diff. peak and hole	0.170 and -0.174 e.Å <sup>-3</sup>	



**Figure S8.** Molecular structure of **1**. Calculated hydrogen atoms are omitted for clarity. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level. Red = oxygen, black = carbon.

**Table S2.** Crystal data and structure refinement for quinone methide **2H** (CCDC-1993086).

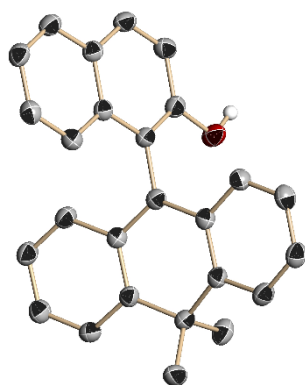
Empirical formula	C <sub>23</sub> H <sub>16</sub> O <sub>1</sub>	
Formula weight	308.38	
Temperature	123(2) K	
Wavelength	0.71075 Å	
Crystal system	orthorhombic	
Space group	P 21/n	
Unit cell dimensions	a = 9.3347(13) Å	$\alpha = 90^\circ$
	b = 10.0778(14) Å	$\beta = 101.582(3)$
	c = 16.957(3) Å	$\gamma = 90^\circ$
Volume	1562.7(4) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.311 Mg/m <sup>3</sup>	
Absorption coefficient	0.077 mm <sup>-1</sup>	
F(000)	736	
Crystal size	0.500 x 0.260 x 0.200 mm <sup>3</sup>	
Theta range for data collection	3.1 to 27.5°	
Index ranges	-12 ≤ h ≤ 12, -20 ≤ k ≤ 20, -13 ≤ l ≤ 13	
Reflections collected	30752	
Independent reflections	3334 [R <sub>int</sub> = 0.0141]	
Completeness to theta = 25.242°	99.8%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.938 and 1.000	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	3334 / 0 / 246	
Goodness-of-fit on F <sup>2</sup>	1.040	
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0332, wR <sub>2</sub> = 0.0833	
R indices (all data)	R <sub>1</sub> = 0.0448, wR <sub>2</sub> = 0.0849	
Largest diff. peak and hole	0.255 and -0.170 e.Å <sup>-3</sup>	



**Figure S9.** Molecular structure of **2H**. Calculated hydrogen atoms are omitted for clarity. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level. Red = oxygen, black = carbon.

**Table S3.** Crystal data and structure refinement for **2H-HBF<sub>4</sub>** (CCDC-1993087).

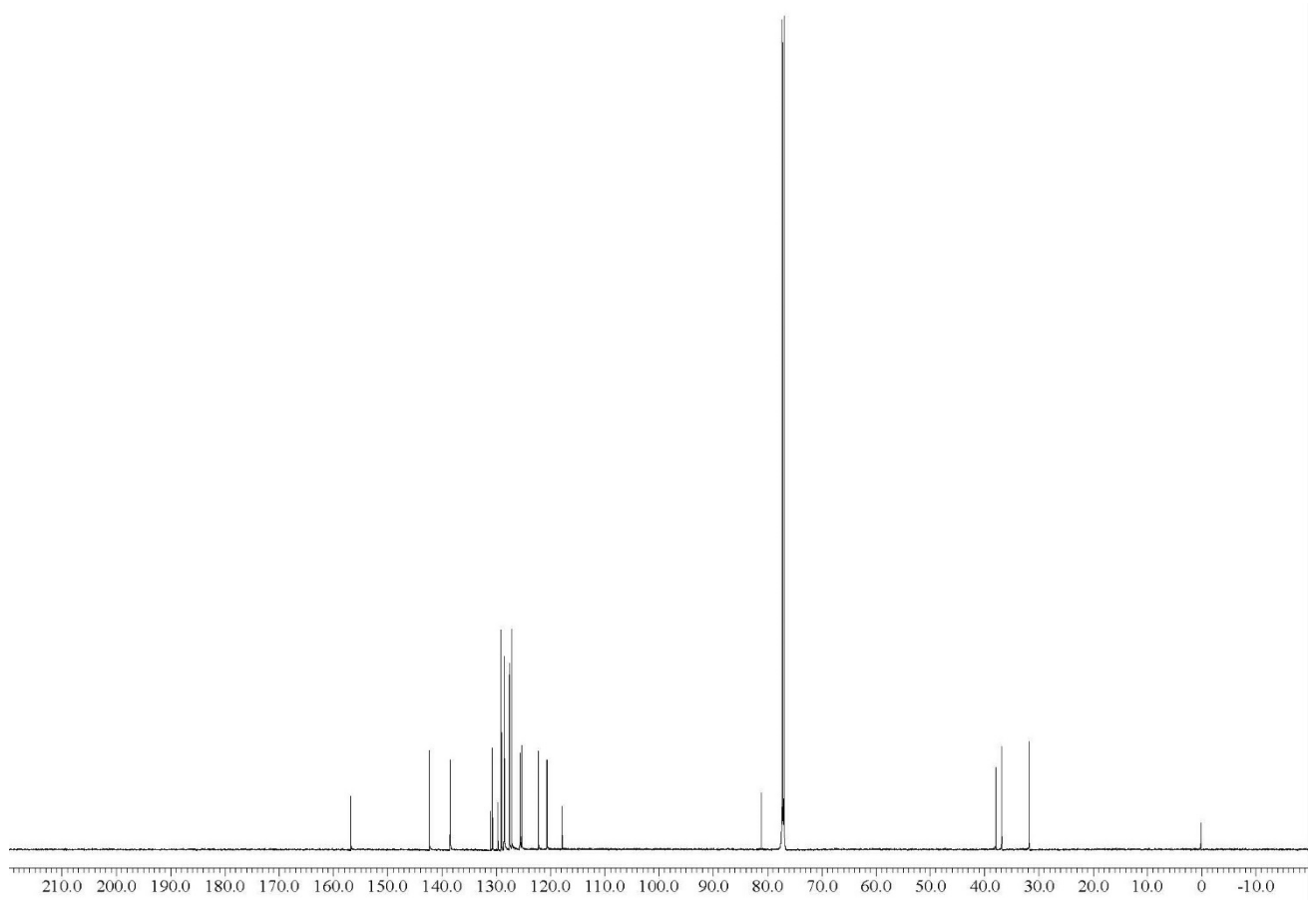
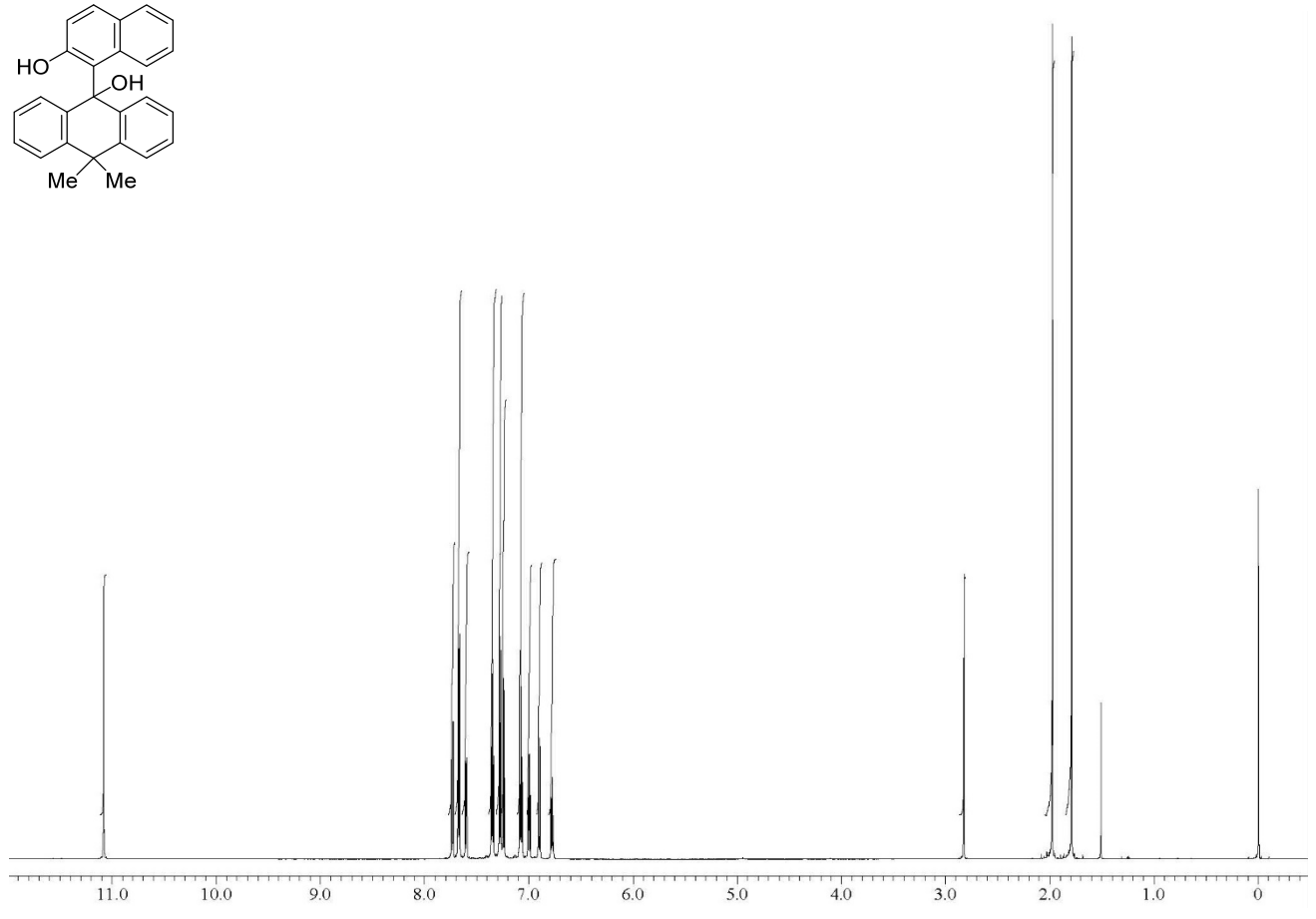
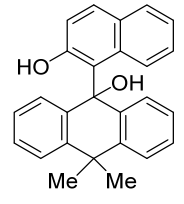
Empirical formula	C <sub>26</sub> H <sub>21</sub> B <sub>1</sub> F <sub>4</sub> O <sub>1</sub>
Formula weight	436.26
Temperature	123(2) K
Wavelength	1.54187 Å
Crystal system	monoclinic
Space group	P 21/n
Unit cell dimensions	a = 7.49820(10) Å      α = 90° b = 19.0172(4) Å      β = 99.675(7) c = 14.6488(3) Å      γ = 90°
Volume	2059.13(8) Å <sup>3</sup>
Z	4
Density (calculated)	1.407 Mg/m <sup>3</sup>
Absorption coefficient	0.911 mm <sup>-1</sup>
F(000)	904
Crystal size	0.10 x 0.050 x 0.050 mm <sup>3</sup>
Theta range for data collection	3.844 to 68.165°
Index ranges	-9 ≤ h ≤ 8, -22 ≤ k ≤ 22, -17 ≤ l ≤ 17
Reflections collected	22984
Independent reflections	3738 [R <sub>int</sub> = 0.0513]
Completeness to theta = 67.687°	99.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7492 and 1.000
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3738 / 0 / 292
Goodness-of-fit on F <sup>2</sup>	1.054
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0408, wR <sub>2</sub> = 0.1024
R indices (all data)	R <sub>1</sub> = 0.0589, wR <sub>2</sub> = 0.1100
Largest diff. peak and hole	0.169 and -0.243 e.Å <sup>-3</sup>



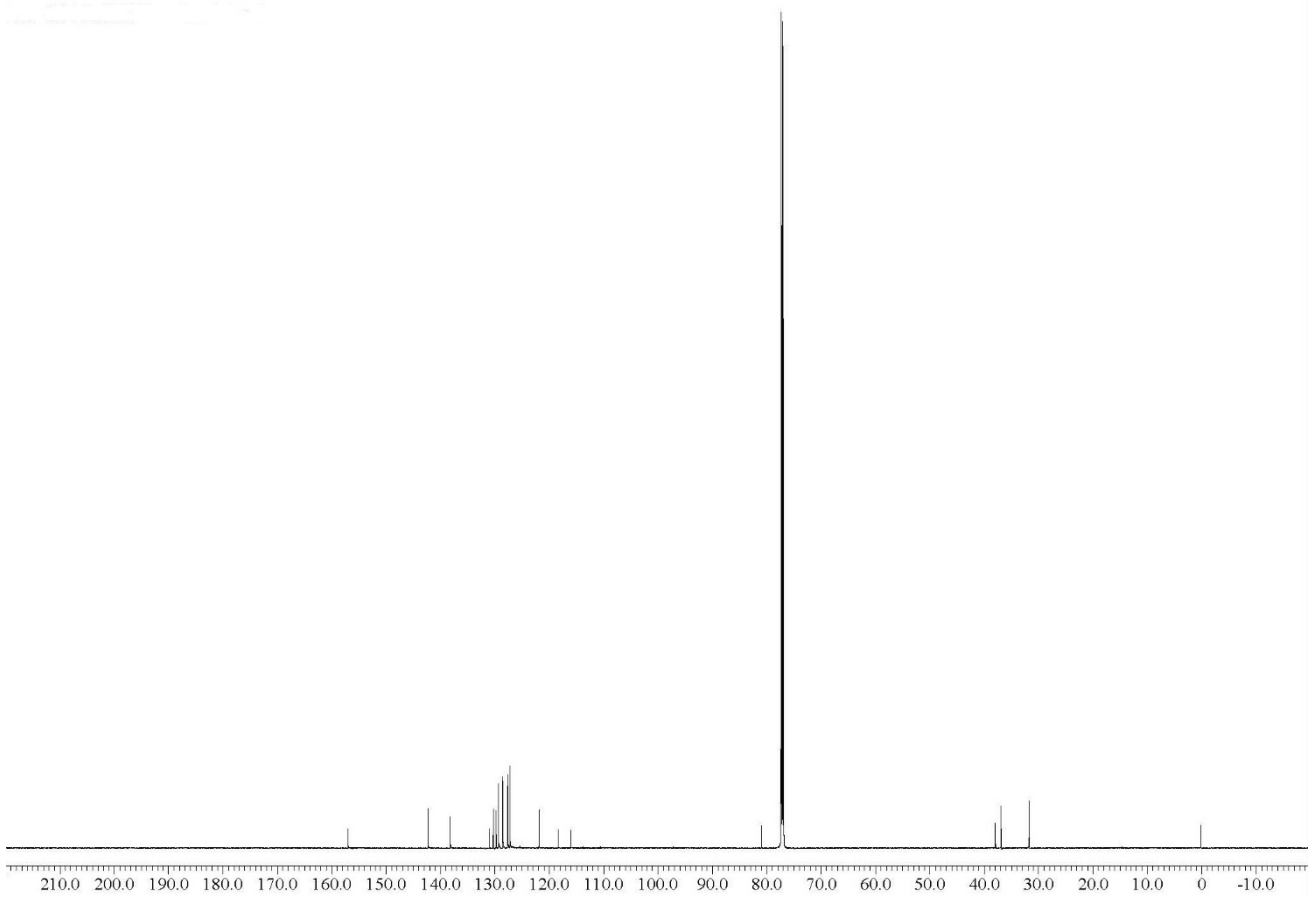
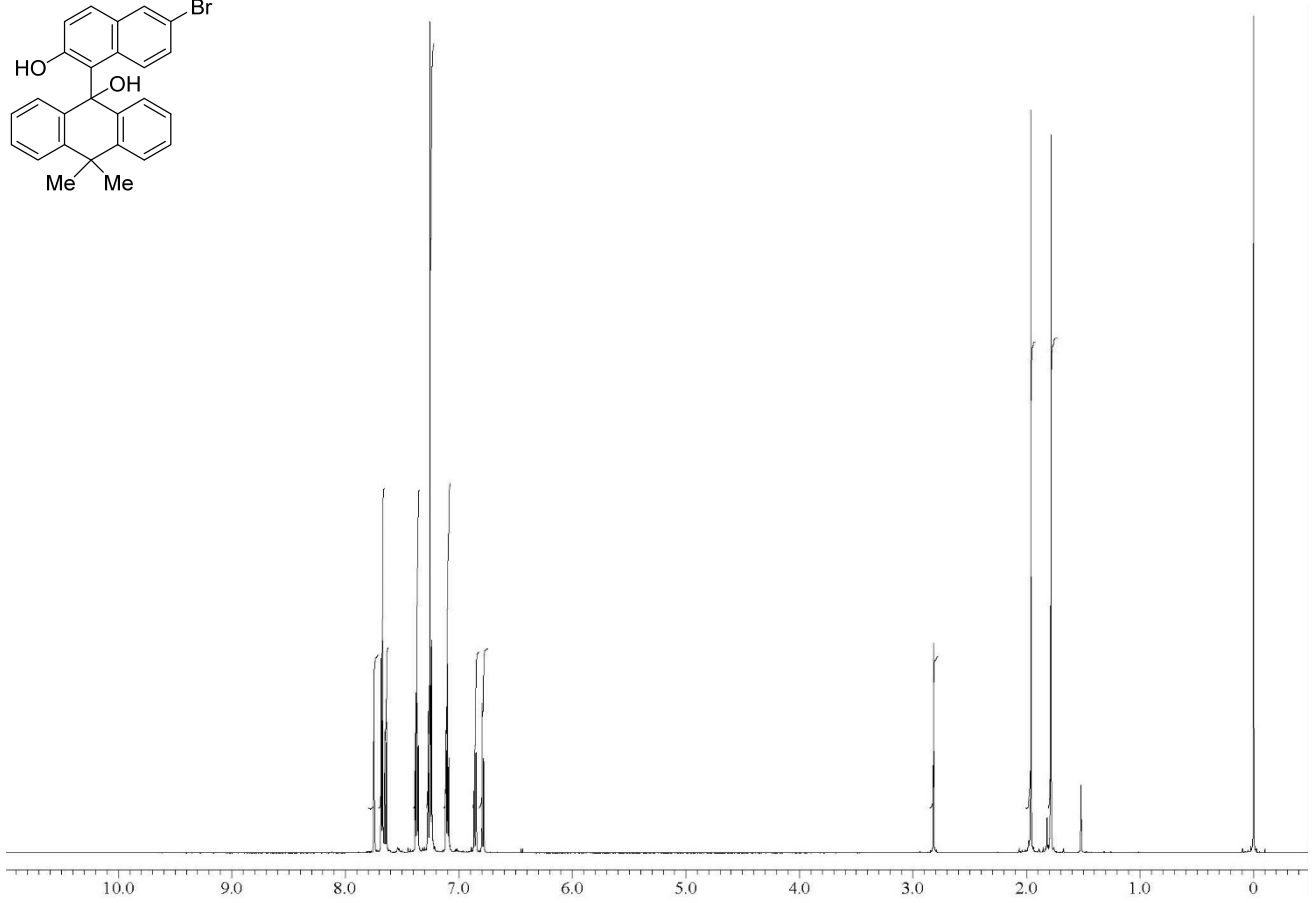
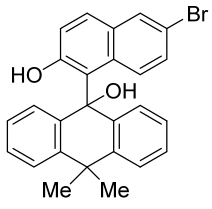
**Figure S10.** Molecular structure of **2H-HBF<sub>4</sub>**. Calculated hydrogen atoms and BF<sub>4</sub><sup>-</sup> are omitted for clarity. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level. Red = oxygen, black = carbon.

Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra:

2H-H<sub>2</sub>O

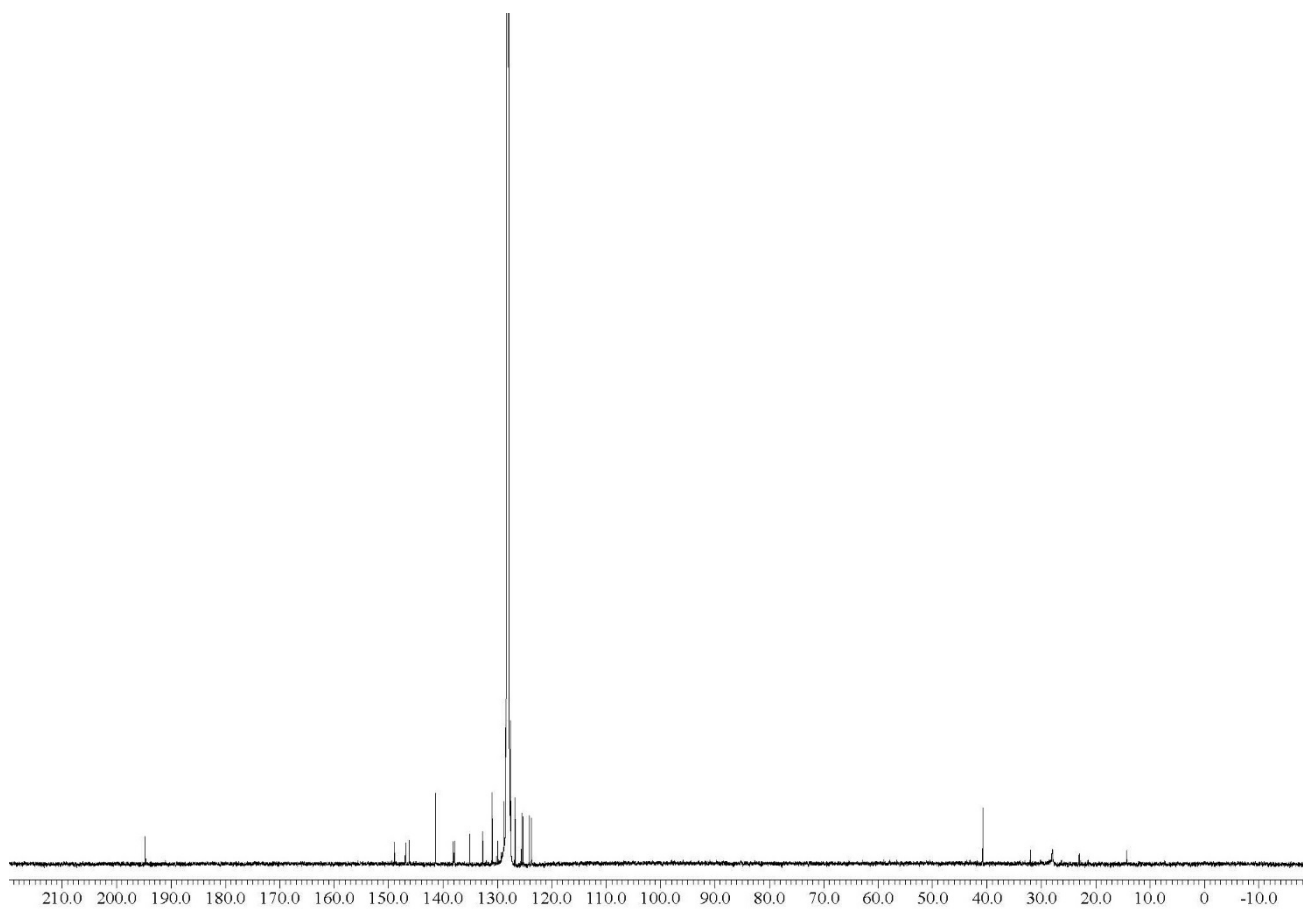
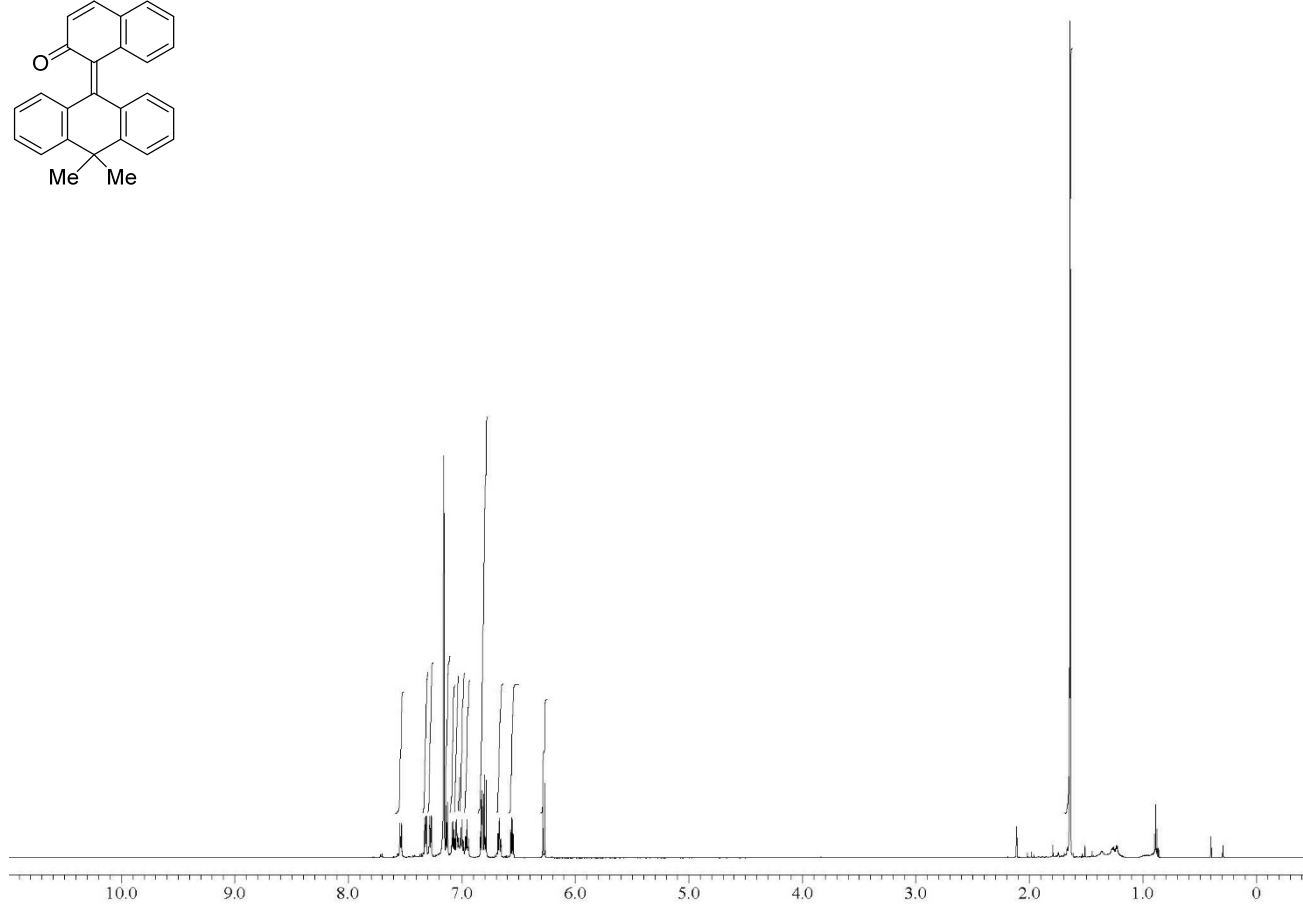
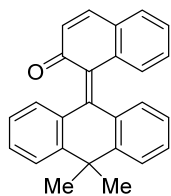


2Br-H<sub>2</sub>O

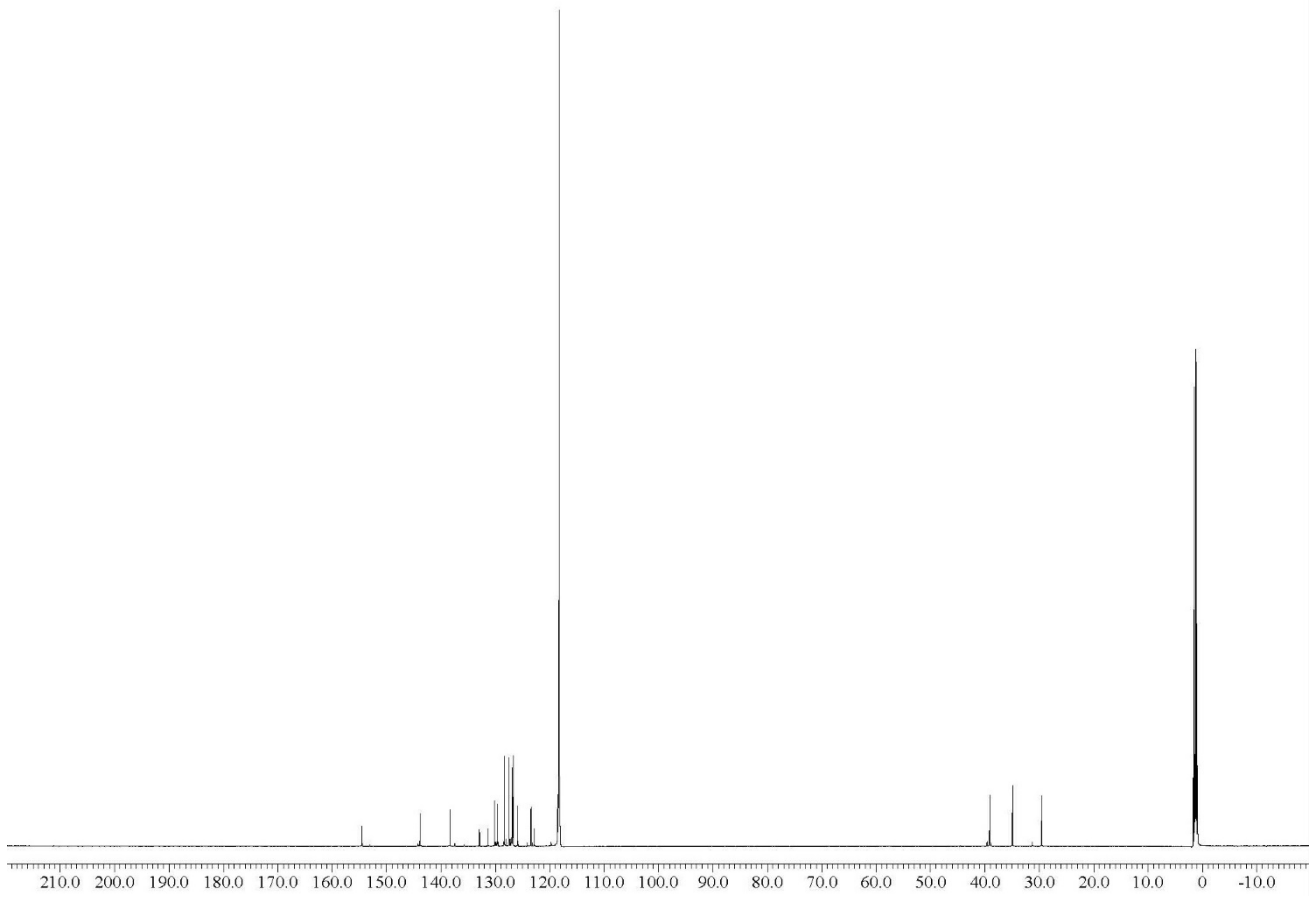
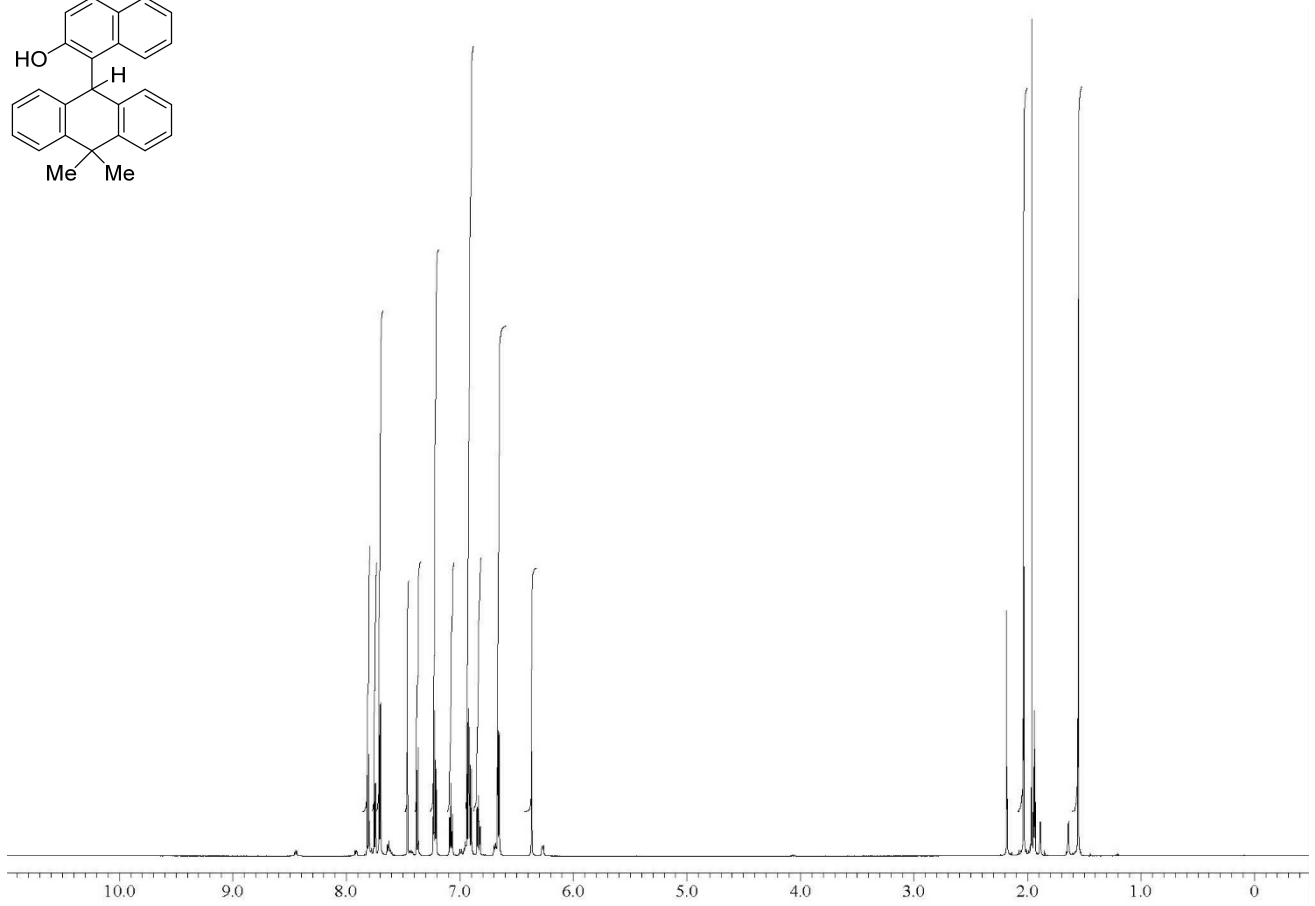
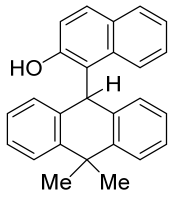




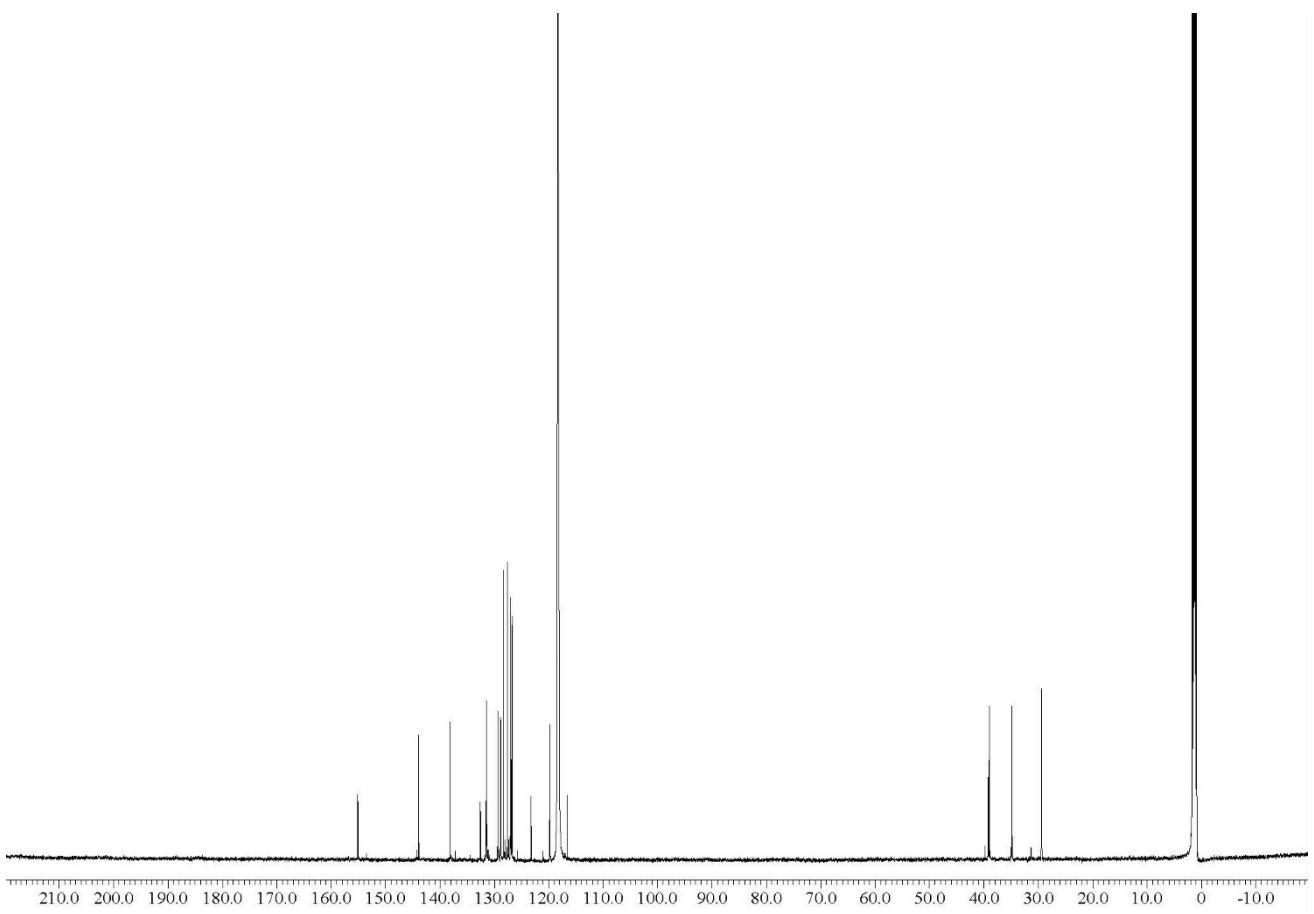
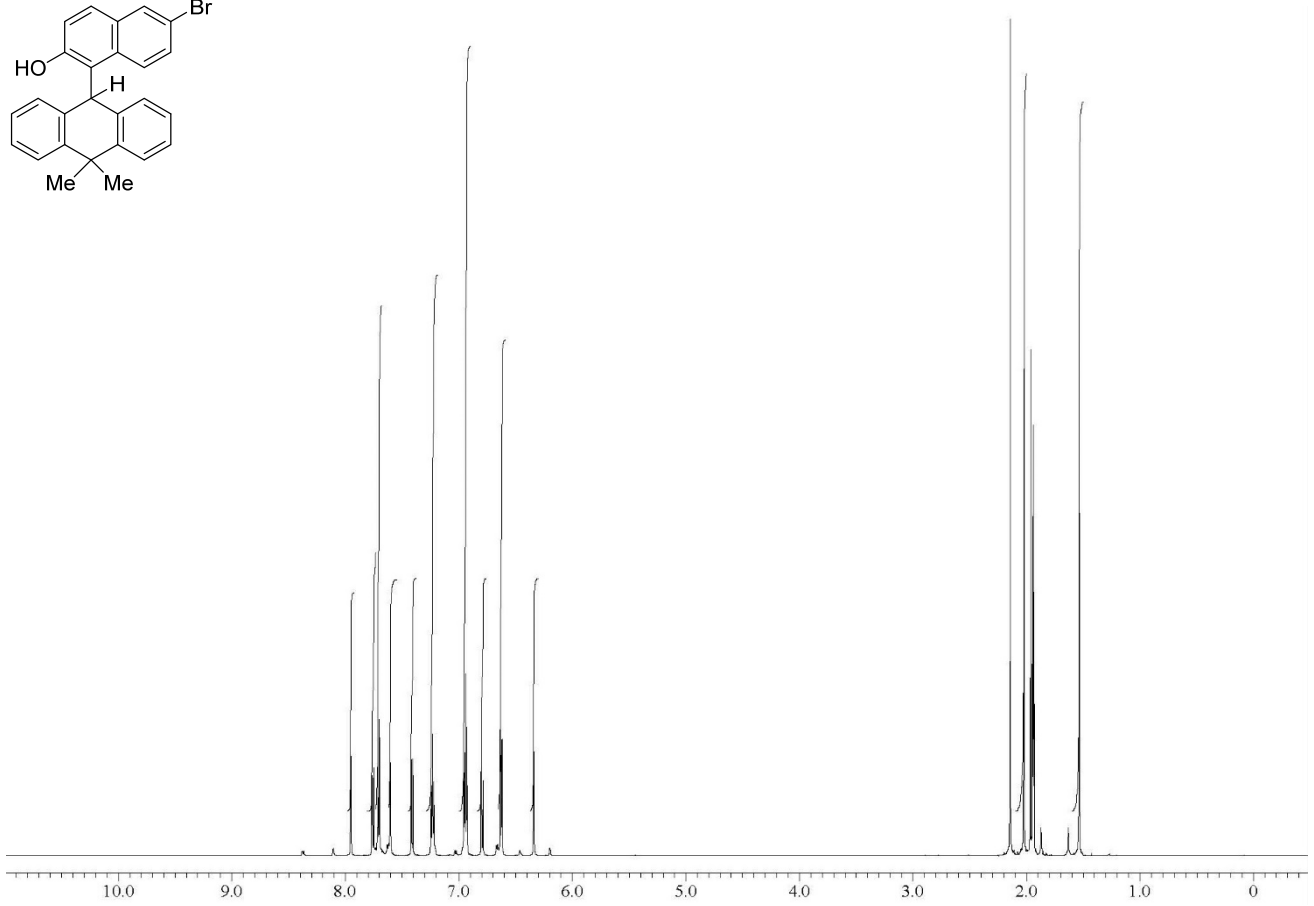
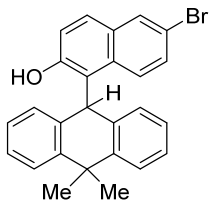
2H



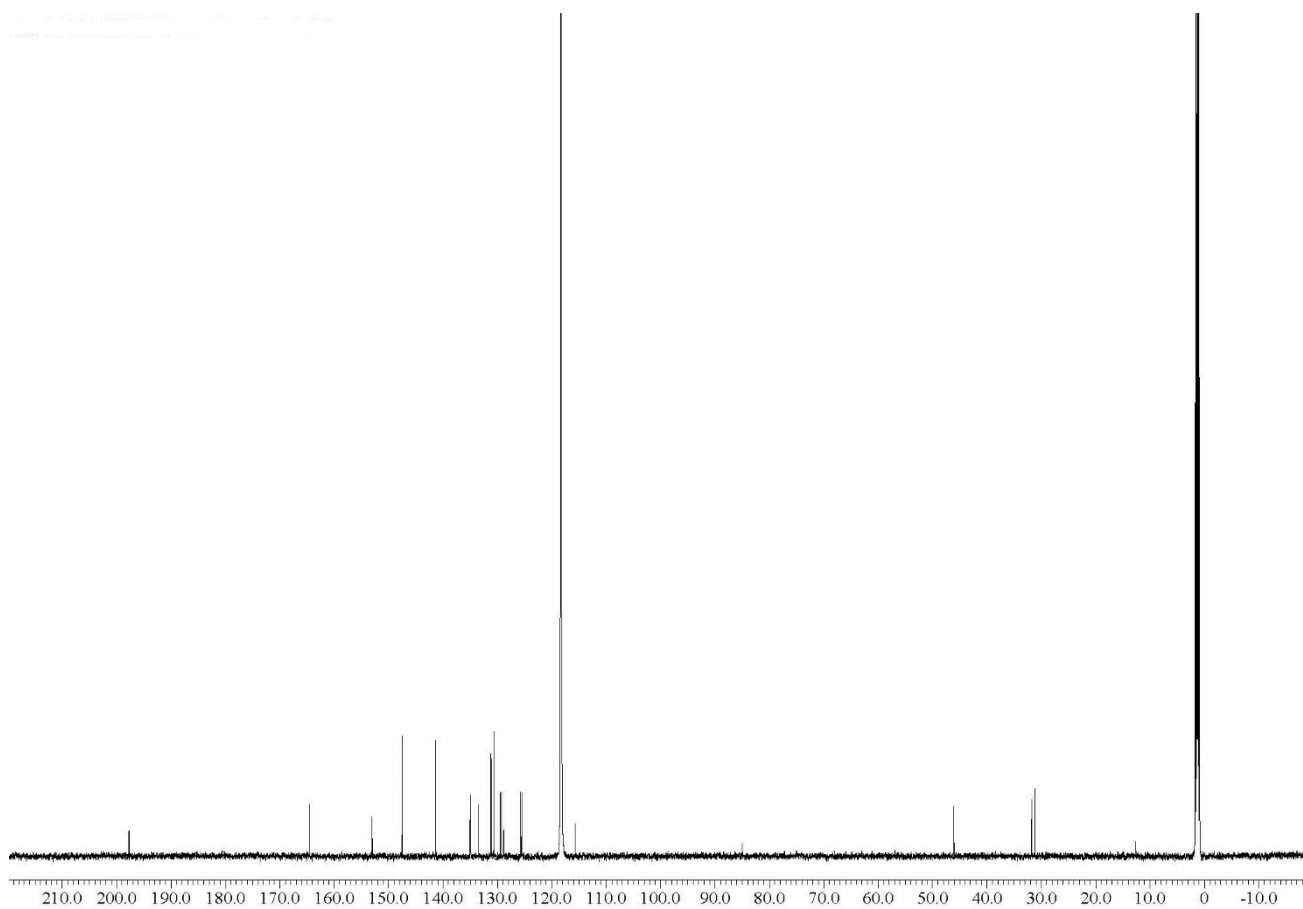
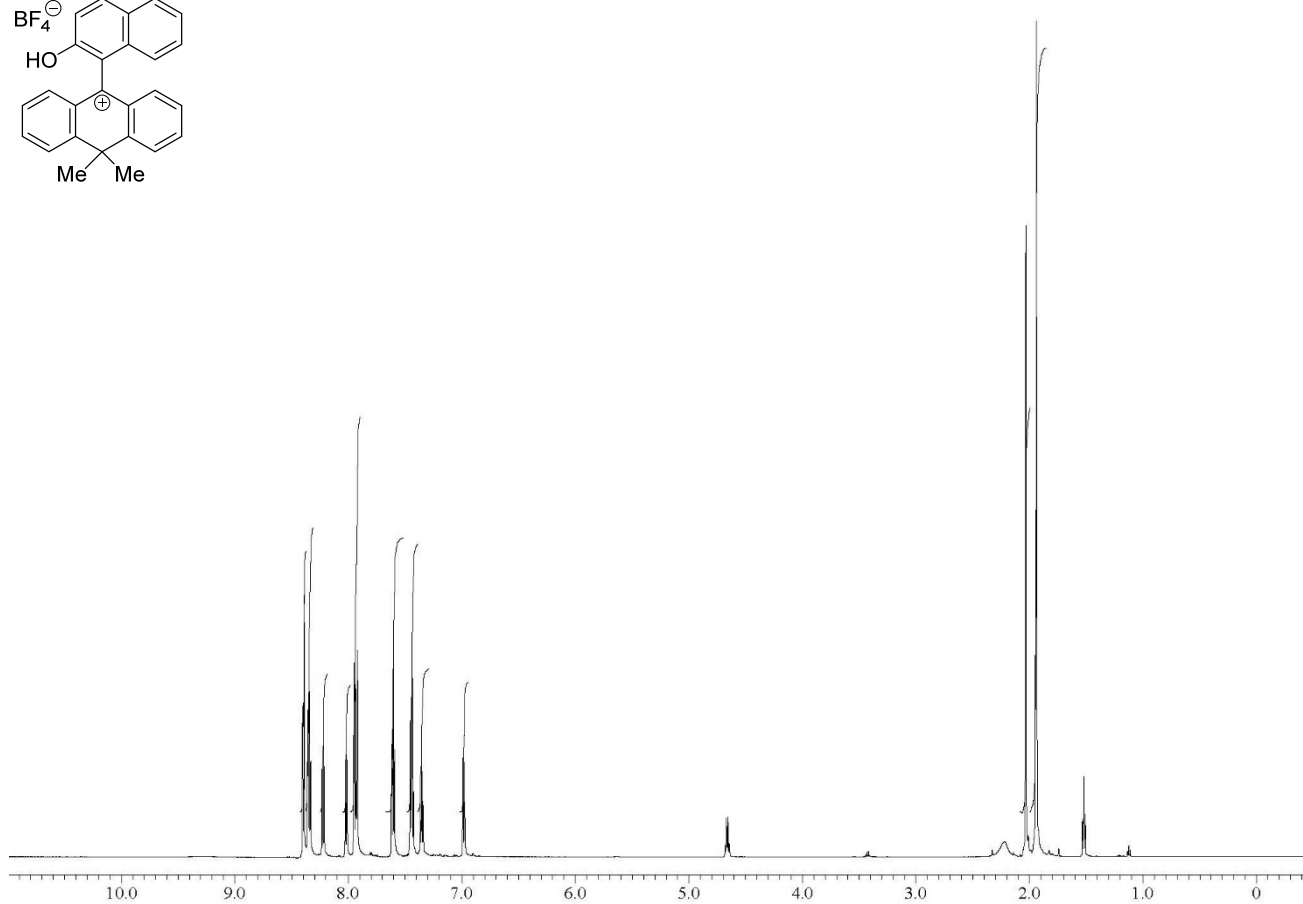
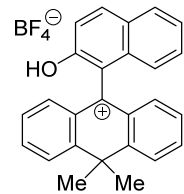
2H-H<sub>2</sub>



2Br-H<sub>2</sub>



**2H-HBF<sub>4</sub>**



2H-HOTf

